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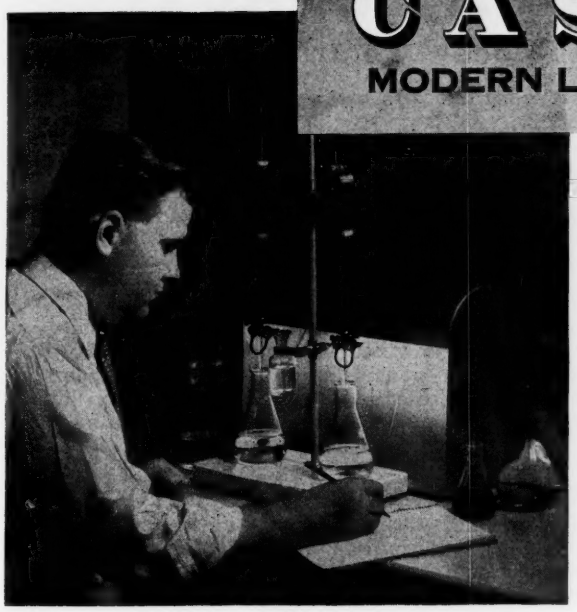

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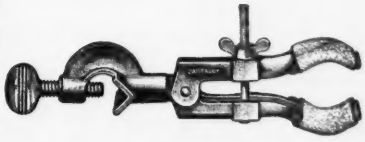

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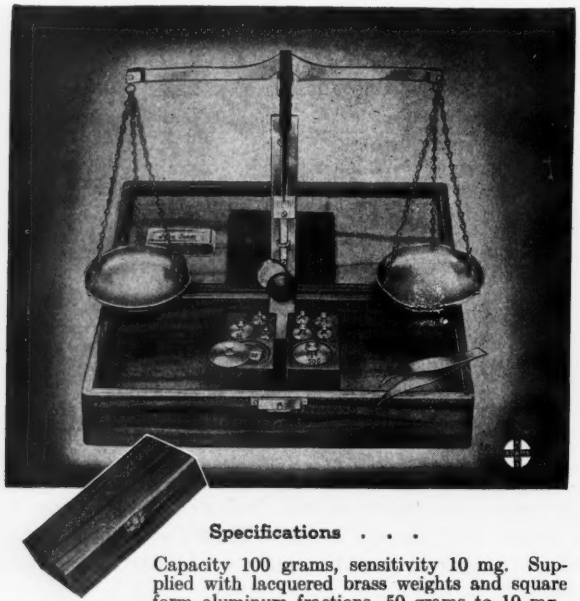

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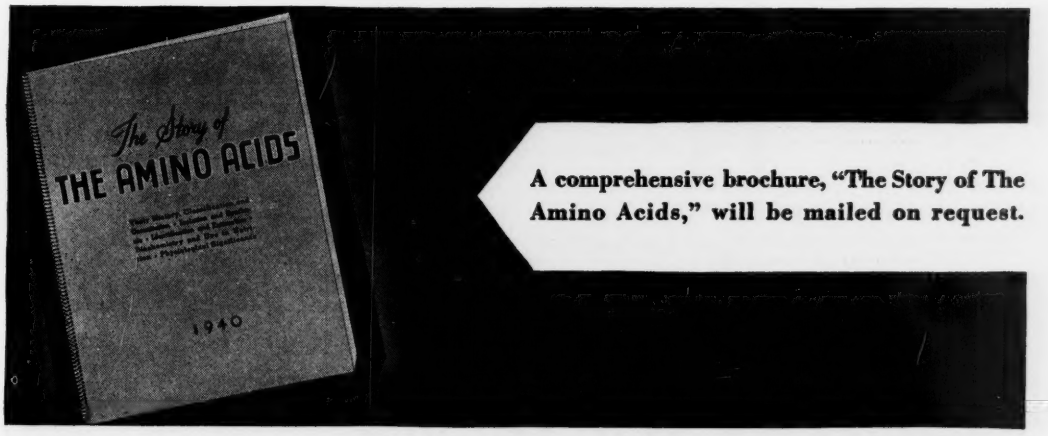

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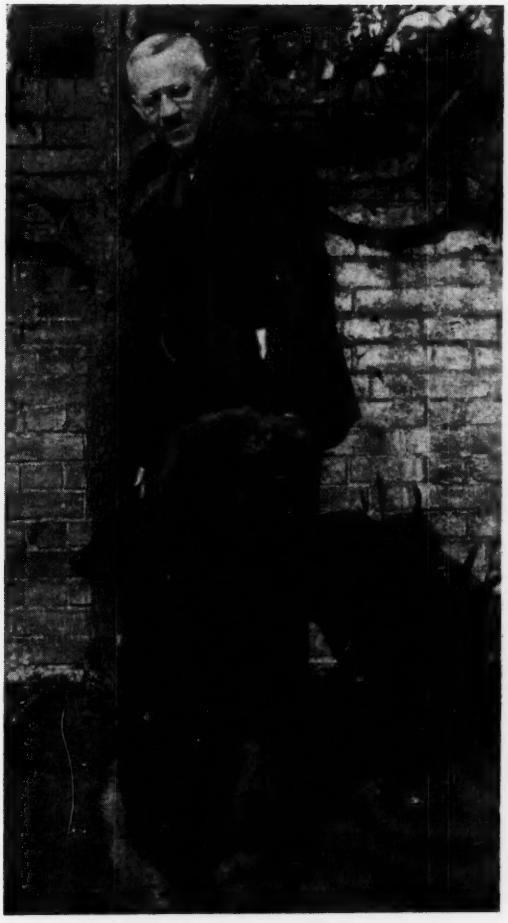

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(For biographical sketch of Thomas Martin Lowry, see page 115.)

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Editor's Outlook

WE HAVE just received a published progress report by the Commission on Teacher Education, founded by the American Council on Education early in 1938. Progress in this "area" will always be good news to us. Naturally, the problems cover a wider range than the mere field of chemical education, but we have a right to a certain amount of attention, at least. We hope that the activities of this commission may in some way serve to alleviate the tension which has long existed among us. We refer, of course, to the relative emphasis in teacher training upon professional subject matter and the so-called "requirements in education." We are not very optimistic in this hope, however. The burden of proof is not entirely one-sided; a deal of compromising must be done. The report of the A. C. S. Committee on Teaching of High-School Chemistry[1] shows this very clearly.

The Commission lists a number of specific questions which it proposes to investigate. Chiefly, these reflect the dominating interest in primary, or at most secondary, teaching. We find, among others:

"How may the teacher grow in understanding and grasp of the social scene, in ability to share democratically in the life of the community, and in skill in fostering the local integration of school and community livings?"

"How may democratic procedures of administration be used in colleges and school systems to develop responsible personality?"

As educational phraseology goes these are not too difficult to understand and we can agree that we would like to have answers, if possible. Going further, we find, indeed, some appeasement to the subject-matter emphasizers:

"How may the teacher's total education, . . . with general or specialized emphases, best be planned and integrated?"

"How may prospective and active teachers be most effectively stirred to take personal responsibility for their own continuous development and aided in planning to this end?"

Perhaps this isn't much, but at least it implies a serious concern in the teacher's intellectual equipment. We could scarcely expect to find the blunt question: "How can the teacher be trained or equipped to teach chemistry most effectively?" That question, it is implied, should be asked and answered by the teacher himself. Personally, we think it ought not to be left entirely without external checks and balances. We admit some concern in the lot of the secondary-school teacher and would only suggest that as much attention be given to his continued advancement in the field of his specialty as to his awareness of current developments in general education. Machinery for the latter purpose is often rather effective.

We would feel more certain of our ground if the training of chemists were the only educational problem concerned. The old principles and practices of apprenticeship still apply to a large extent; the master chemist is the one best qualified to train and instruct his successor. The voice of the American Chemical Society, for example, should be heard and respected in the matter of the professional curriculum.

But other interests must be served and we must either permit the professional "educationists" to have a hand in the proceedings or we must clearly show ourselves able to discharge our larger educational responsibilities. As long as there remains the least measure of truth in the assertion that subject-matter specialists are too narrow in their viewpoints we will have strife. A greater will to coöperate should resolve the difficulty, however.

But chemical education finds its principal field at the higher educational level. And it is precisely here that any effort at the regulation of teacher training meets the greatest resistance. This may or may not have any bearing on the fact that the standards of teaching at this level are in some respects lower than those at the secondary level.

Since this last statement will very likely be challenged, let us say that what we have in mind is the fact that, compared with the high-school teacher, the college instructor is generally less aware of and concerned with the bearing of his own particular bit of instruction upon the general aims of the educational process. When this is true we think it implies a lower standard of teaching.

That there has been very little regulation of teacher training at the college level may be due to the indolence or the willful neglect of the "employers" of college teachers to do the job themselves, or to the modesty, timidity, or simple inability of the usual regulative agencies to invade this field.

To be effective this effort must be organized by the colleges themselves and it is encouraging to note that they are represented on the Commission, eleven institutions being listed among the "coöperating units." This aspect of the study was only opened up during the last few months and we hope that its relegation to the closing paragraph of the report is not an indication of its relative importance in the whole scheme. We really want to see something come out of this and hope that results, if and when they emerge, will not be lost in a verbal shuffle.

[1] *Ind. Eng. Chem.* (*News Ed.*), **14**, 147 (Apr. 20, 1936).

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What's Been Going On

Synthesis of Surface-Active Agents

THE role of surface-active agents in modern life becomes apparent from the tabulation of over 280 such products by Van Antwerpen in the January issue of *Industrial and Engineering Chemistry*, pp. 16–22. There is no doubt that the use of ordinary soap as a detergent and wetting agent is being supplanted to an appreciable degree by these new synthetic organic chemicals.

These synthetic surface-active agents are in general similar to soap in that they contain a solubilizing group and a hydrocarbon chain (or ring with a side chain) of variable length. The solubilizing group in each case is water-attracting or hydrophilic, whereas the hydrocarbon portion of the molecule is water-repelling or hydrophobic. The combination of these two properties, in the same molecule, makes a compound active at the interface between two liquids by effecting reduction of the surface tension.

Langmuir has suggested that, at the interface between two immiscible liquids, the hydrocarbon portion of these surface-active agents becomes oriented toward the hydrophobic media whereas the other portion of the molecule is aligned toward the hydrophilic material. The behavior of any given compound will depend, accordingly, on the components of the interface. If the interface is made up of two water-repelling or hydrophobic compounds, obviously the direction of orientation is not so readily predictable.

It is apparent, therefore, that the properties of a surface-active agent may be varied more or less as desired by changing the water-repelling properties (or length) of the hydrocarbon residue and/or modifying the water-attracting properties (or nature) of the solubilizing group. The extensive list of compounds with surface-active properties, previously mentioned, serve as specific examples of ways of effecting these modifications.

The nature of the hydrocarbon residue in these surface-active compounds is determined largely by availability. When the hydrocarbon portion of the molecule is aliphatic, the chain is not branched in most cases because of the relative cheapness of the continuous chain compounds. When the hydrophobic portion of the molecule is of the aromatic or substituted aromatic type, the alkyl and/or aryl substituents on the aromatic nucleus offer a number of possible variations.

Some of the more commonly used solubilizing or hydrophilic groups are carboxyl ($\cdot CO_2H$), bisulfate [$\cdot O \cdot S(\rightarrow O)_2 \cdot OH$], dihydrogenphosphate [$\cdot O \cdot P(\rightarrow O)(OH)_2$], hydroxyl ($\cdot OH$), and sulfonic acid [$\cdot S(\rightarrow O)_2 \cdot OH$], all of which have a solubilizing effect that is somewhat characteristic of the group.

For convenience, some of the more important types of these surface-active agents may be tabulated as:

Type		*General Formula*	*Name or Description*
A.	1.	$R \cdot CO \cdot O^-{}^+Na$	Salt of a fatty acid
	2.	$C_nH_{2n-5}(\cdot O \cdot SO_2 \cdot O^-{}^+Na)CO \cdot O^-{}^+Na$	Disodium salt of sulfated fatty acid
	3.	$R \cdot CO \cdot O \cdot CH_2 \cdot CHOH \cdot CH_2 \cdot OH$	Glyceryl ester of a fatty acid
	4.	$R \cdot CO \cdot O \cdot CH_2 \cdot CH_2 \cdot SO_2 \cdot O^-{}^+Na$	Sodium fatty-acid-ester-sulfonate
	5.	$R \cdot CO \cdot NH \cdot CH_2 \cdot CH_2 \cdot SO_2 \cdot O^-{}^+Na$	Sodium fatty-acid-amide-sulfonate
	6.	$R \cdot CO \cdot NH \cdot CH_2 \cdot CH_2 \cdot NR_2$	Fatty acid amidodialkylamine
B.	1.	$R \cdot O \cdot SO_2 \cdot O^-{}^+Na$	Sodium alkyl sulfate, where R is large
	2.	$R'_2CH \cdot O \cdot SO_2 \cdot O^-{}^+Na$	Sodium secondary alkyl sulfate
	3.	$R' \cdot O \cdot OC \cdot CH_2$ $R' \cdot O \cdot OC \cdot CH \cdot O \cdot SO_2 \cdot O^-{}^+Na$	Sodium salt of the bisulfate of a dialkyl dicarboxylate
C.	1.	$R \cdot SO_2 \cdot O^-{}^+Na$	Sodium alkyl sulfonate, where R is large
	2.	$Ar \cdot SO_2 \cdot O^-{}^+Na$	Sodium aryl sulfonate
	3.	$R' \cdot O \cdot OC \cdot CH_2$ $R' \cdot O \cdot OC \cdot CH \cdot SO_2 \cdot O^-{}^+Na$	Sodium salt of the sulfonic acid derivative of a dialkyl dicarboxylate
D.	1.	$R \cdot N^+$	An alkyl pyridinium salt, where R is a long aliphatic chain

In this tabulation the symbol R represents a long hydrocarbon chain of the aliphatic type, Ar signifies an aryl or aromatic residue, and R′ is a primary or secondary alkyl group of comparatively low molecular weight.

Specific examples of each of these types are:

A. 1. Ordinary soap or sodium stearate, $CH_3 \cdot (CH_2)_{16} \cdot CO \cdot O^-{}^+Na$
2. The sodium salt of the sulfated derivative of ricinoleic acid, $CH_3 \cdot (CH_2)_5 \cdot CH(O \cdot SO_2 \cdot O^-{}^+Na) \cdot CH_2 \cdot HC{:}CH \cdot (CH_2)_7 \cdot CO \cdot O^-{}^+Na$
3. Glyceryl oleate, $CH_3 \cdot (CH_2)_7 \cdot HC{:}CH \cdot (CH_2)_7 \cdot CO \cdot O \cdot CH_2 \cdot CHOH \cdot CH_2 \cdot OH$
4. Igapon A, $CH_3 \cdot (CH_2)_7 \cdot HC{:}CH \cdot (CH_2)_7 \cdot CO \cdot O \cdot CH_2 \cdot CH_2 \cdot SO_2 \cdot O^-{}^+Na$
5. Igapon T, $CH_3 \cdot (CH_2)_7 \cdot HC{:}CH \cdot (CH_2)_7 \cdot CO \cdot NH \cdot CH_2 \cdot CH_2 \cdot SO_2 \cdot O^-{}^+Na$
6. A sapamine, $CH_3 \cdot (CH_2)_7 \cdot HC{:}CH \cdot (CH_2)_7 \cdot CO \cdot NH \cdot CH_2 \cdot CH_2 \cdot N(CH_2 \cdot CH_3)_2$

B. 1. Sodium cetyl sulfate, $CH_3 \cdot (CH_2)_{15} \cdot O \cdot SO_2 \cdot O^-{}^+Na$
2. Sodium *sec*-decyl sulfate, $CH_3 \cdot (CH_2)_7 \cdot CH(O \cdot SO_2 \cdot O^-{}^+Na) \cdot CH_3$
3. The sodium salt of the sulfated derivative of dioctyl malate, $CH_3 \cdot (CH_2)_6 \cdot CH_2 \cdot O \cdot OC \cdot CH(O \cdot SO_2 \cdot O^-{}^+Na) \cdot CH_2 \cdot CO \cdot O \cdot CH_2 \cdot (CH_2)_6 \cdot CH_3$

C. 1. Sodium lauryl sulfonate, $CH_3 \cdot (CH_2)_{10} \cdot CH_2 \cdot SO_2 \cdot O^-{}^+Na$
2. Sodium laurylbenzene sulfonate, $CH_3 \cdot (CH_2)_{10} \cdot CH_2 \cdot C_6H_4 \cdot SO_2 \cdot O^-{}^+Na$
3. Aerosol O. T. Dry, $C_8H_{17} \cdot O \cdot OC \cdot CH(SO_2 \cdot O^-{}^+Na) \cdot CH_2 \cdot CO \cdot O \cdot C_8H_{17}$

D. 1. Laurylpyridinium chloride, $CH_3 \cdot (CH_2)_{10} \cdot CH_2 \cdot C_5H_4NH^+{}^-Cl$

Of these several types of surface-active agents, probably the most commonly used domestically are of the C. 1 type, to which presumably belong Cue, dreft, drene, Irium, and Teel. Cue is doubtless a salt of an alkyl sulfonic acid, dreft contains sodium lauryl sulfonate as the principal ingredient, drene is the triethanolamine salt of lauryl sulfonic acid suspended in an inert medium, Irium is advertised as the sodium salt of an alkyl sulfonic acid, and Teel is no doubt a salt of an alkyl sulfonic acid.

—ED. F. DEGERING

Barium for Bearings

From the research laboratories of the General Electric X-ray Corporation comes the announcement of the solution of a difficult lubrication problem. To lubricate a rotor operating in a vacuum in an X-ray tube oils and greases are not permissible because of their high vapor pressures. It was found that when a thin film of metallic *barium* was applied to the bearing, the speed of the rotor rose to over 3500 R.P.M., the noise was reduced, and the coasting time was increased from 12 seconds to eight minutes.

—LAURENCE S. FOSTER

Toluene from Petroleum

The first petroleum toluene refinery has just recently been put in operation in Houston, Texas, by the Shell Oil Company. The new process will help prevent recurrence of the serious bottleneck caused during the World War by limited facilities for recovering toluene from coal tar. The plant at Houston will produce over 2,000,000 gallons annually, from which it is possible to produce about 20,000,000 pounds of TNT.

Thiourea

Thiourea (thiocarbamide) went into commercial production for the first time in the United States in 1940. This compound is used as an intermediate in making thiamine chloride (vitamin B_1) and sulfathiazole, 2-sulfanilyl-amino-thiazole, one of the newest additions to the sulfanilamide family of drugs. Other members of this family, produced during the last year and undergoing exhaustive tests before being released, are sulfadiazine (sulfanilyl-amino-pyrimidine) and sulfaguanidine (sulfanilyl-guanidine). The latter has attracted special attention because of its extraordinary value as an intestinal disinfectant.

(*Continued on page 133.*)

Foundation and Development of the Gas Industry in America[1]

CHANNING W. WILSON

Consolidated Gas Electric Light and Power Company of Baltimore, Baltimore, Maryland

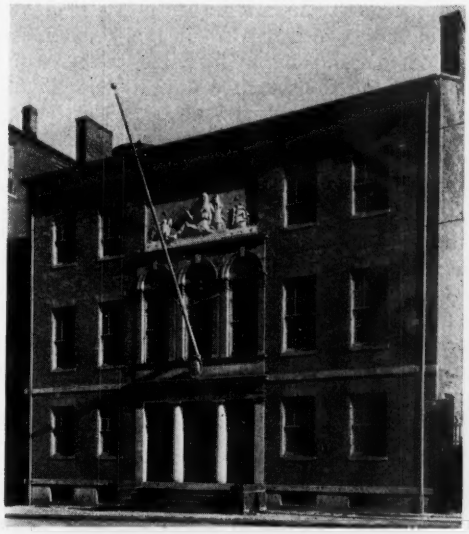
THE discovery of coal gas was made by Jan Baptista van Helmont in 1609, when he found that upon heating coal and wood ". . . did belch forth a wild spirit or breath. This spirit . . . I call by the name of gas." Not until 1792, however, was this "wild spirit" put to practical use, when William Murdock, in Cornwall, England, lighted his own house with gas made from coal in an iron retort. Murdock, a man with an active, inventive mind, experimented with the distillation of coal while he was employed by James Watt in the construction of steam engines at Birmingham, England. Many other requisites of the process, to make it commercially applicable, also received his attention, such as methods for storing, purifying, and distributing the product.

Although Phillipe Lebon performed experiments in France at about the same time, and received a patent in 1799 on a manufacturing process, it is generally agreed that Murdock was the first to make a practical application of gas for illumination.

Demonstrations of the use of gas for illuminating buildings as Murdock had done were shortly made in several countries, but it was in England again, in 1812, that the first gas manufacturing company in the world was established to provide the city of London with gas illumination.

Baltimore first saw gas illumination in the early part of the year 1802, when Benjamin Henfrey, an Englishman, lighted "Mr. Robardett's ballroom, Second Street, on the falls" with gas made by distilling a mixture of Baltimore coal and wood. "A suspended chandelier lamp for six lights" was among the fixtures so exhibited. His exhibition did not, apparently, meet with great public interest and support, for not until fourteen years later was such an enterprise to take on commercial aspects in America. In the meantime, the London and Westminster Gas Light and Coke Company received a royal charter in April, 1812, to become the first gas company in the world. Soon London streets began to be lighted with gas flames. Homes of wealthy people and business houses were not far behind.

By 1816 enough news of the amazing illumination of London had filtered back to America that popular interest was easy to arouse when Rembrandt Peale lighted his museum on Holliday Street in Baltimore with gas made in a small plant back of this building. Both of these buildings are still standing. Peale's showmanship was probably as greatly responsible as his business acumen for the rapid progress made in the formation of a company to exploit this new field of enterprise. The first gas manufacturing company in America, which was the second in the world, grew directly from the interest in these demonstrations at the museum. Its founders were Rembrandt Peale,



Courtesy of the Consolidated Gas Electric Light and Power Company of Baltimore

THE PEALE MUSEUM TODAY, HOLLIDAY STREET, BALTIMORE

William Lorman, James Mosher, Robert Cary Long, and William Gwynn. On June 17, 1816, only four days after Peale's first exhibition, the City Council passed an ordinance authorizing the Mayor of Baltimore to contract for lighting the city by means of gas, and another empowering the Gas Light Company of Baltimore to lay pipes in the streets, squares, lanes, and alleys of the city for that purpose. This company was incorporated the following year, on February 5, 1817, and twelve days later the first gas street lamp in Baltimore was lighted.

In this manner, Baltimore became the cradle of one of the country's important chemical industries. In the one hundred twenty-two intervening years, the industry has expanded throughout the country so that there are few families, rich or poor, living in cities who do not in some manner come into intimate contact with it.

Coal gas was first made for public use in Baltimore at the "Davis Street works" of the Baltimore Gas Light

[1] Presented before the Division of History of Chemistry at the ninety-seventh meeting of the A. C. S., Baltimore, Maryland, April 5, 1939.

Company. This plant was located on Saratoga Street between Davis Street and Guilford Avenue. It was the first complete gas works in America. In 1847 a new plant was built on Holliday Street near Peale's Museum, and was used until 1861. In 1856, the site of the present plant at Spring Gardens, in the southern part of the city, was selected for the next "new" plant, and gas has been supplied to the people of Baltimore from this location since then.

The Gas Light Company of Baltimore continued in undisputed control of the gas lighting business in the city until 1871. Between that year and 1888 several small companies sprang up and began to supply gas to various sections of the community. Some had to discontinue operations after a short life, the others by purchase or merger were absorbed into a single organization in 1888, which resulted in the formation of the Consolidated Company. The name was subsequently changed to the Consolidated Gas Electric Light and Power Company of Baltimore after the electric lighting companies and the gas company merged.

In 1870 the People's Gas Company built a coal gas plant, which operated until 1881. In 1877 The Consumer's Mutual Gas Light Company was started for the purpose of supplying water gas made by the Lowe process. The plant was closed down in 1904 by the Consolidated Company. In 1881 The Equitable Gas Light Company erected a plant to produce gas from wood. However, within a short time a water gas plant and later a coal gas plant took the place of the original wood plant. The company operated for only a few years and the plant was closed after combining with the Chesapeake Gas Company in 1885, which had been founded earlier the same year. The Chesapeake Company made water gas by the Jerzmanowski process, in which it was sought to reduce the quantity of poisonous carbon monoxide in the gas by using limestone in the superheaters instead of fire-brick. The Chesapeake Company later combined with the present company, the Jerzmanowski process was abandoned, and the plant was finally closed by 1905. The Suburban Gas Company operated a small coal gas plant in Highlandtown, near Baltimore, from 1903 until 1907, when it was taken over by the Consolidated Company and closed.

The present manufacturing plant is located on the water-front at Spring Gardens. All the gas supplied to the city of Baltimore and the surrounding territory comes through this plant. Coke-oven gas, purchased from the Bethlehem Steel Company, is mixed with carburetted water gas manufactured at Spring Gardens, and with a small amount of refinery oil gas. It is rigorously purified at this plant, stored in large storage holders before distribution through the diverging system of mains and service lines to the consumers.

Seven years after the founding of the Baltimore Company the Boston Gas Light Company was established, in 1823, but its plant was not built and put in operation until 1828. In the meantime, the New York Gas Light Company was formed, in 1825, one of seven gas companies which operated in that city in competition with each other until their consolidation in 1884. Although the first recorded demonstration of gas in the United States was in Philadelphia in 1796, the people of this city fought successfully for many years the innovation in street illumination. Not until 1836 did the use of gas supplant candles, lanterns, and whale-oil lamps for this purpose. The Philadelphia Gas Works was a privately owned company controlled by a board of trustees appointed by the city.

As in most new processes or products, simplicity being the keynote, the early manufacture of illuminating gas required little more than the release of volatile constituents of the raw material by the application of heat. Although we now realize that it is essentially a chemical industry, the first gas plants probably had little use for a trained chemist. A charge of fuel was put into the ovens, whether they were brick or iron, and it was heated until the volatile constituents were gone, the coke removed, and the oven recharged. The fact that the bituminous coal mines of this country were not tapped until 1840, and that coking coal imported from England was very expensive, led some of the early gas plants to use wood, rosin, or mixtures of them with coal. It has already been noted that one of the early companies of Baltimore was begun for the purpose of making gas from wood. In February, 1828, the New York Gas Light Company began converting its oil gas plant to one using rosin according to a patented process developed abroad. Gas from these sources was rich in illuminants, those constituents which readily break down and give a flame of luminous characteristics because of the incandescent carbon particles present therein. A gas flame was the equivalent of sixteen or eighteen standard sperm candles, or twice as many ordinary wax or tallow candles.

The great majority of the gas companies, however, used coal, and in the long run these turned out to be the most successful. It is not clear, prior to 1840, whether native anthracite, semi-anthracite, or imported coal predominated in use, possibly a mixture of imported and native coals.

It is interesting to note at this point that it was not until 1856, nearly half a century after London's streets were lighted with gas, and coal tar was available, that William Henry Perkin discovered the first coal-tar dye.

In the modern coke plant, whether coke or gas is the principal product, the operations are nearly the same as those performed in the first plants, but on a much more extended and elaborate scale. The by-products recovered from the coking operations have become a very important source of revenue, and permit the sale of the gas produced at a much lower price. The great chemical versatility of coke-oven plants is evident from a list of the materials which can be made from the coal.

The next forward step in gas manufacturing processes was the invention by Professor Thaddeus S. C. Lowe of the carburetted water gas process, patented in 1872, generally referred to as the Lowe process. The discovery and exploitation of petroleum and its

products following the drilling of the first well at Titusville, Pennsylvania, in 1859 made the water gas process economically feasible in this country and such an outstanding success.

Professor Lowe had had experience in gas making, on a small scale, when he carried out his experiments on gas-filled balloons during the Civil War. The balloons were inflated with coal gas generated directly on the field of action, and Lowe performed notable service for the Union forces at Fair Oaks, Virginia, in ascending over the lines in a balloon for observational purposes.

Tessie Du Motay, a Frenchman, was also engaged in perfecting, independently of Lowe, a similar form of water gas apparatus at about the same time.

"Blue" water gas, a mixture of hydrogen and carbon monoxide made by decomposing steam on incandescent coke, was not suitable for the open flame burners of the day, since it burned with a blue flame of no illuminating value. By adding oil vapor to the "blue" water gas the missing illuminants were supplied. In brief, the process is as follows. In a cylindrical generator coke is heated to incandescence by blasting it with air, the products of combustion being released to the atmosphere. There ensues a gas making period during which steam is admitted to the generator and the endothermal decomposition reaction takes place. Into another heated chamber, called the carburettor, which is filled with fire-brick, the "blue" gas passes, where it is enriched by a spray of oil. The heat vaporizes and partially cracks the oil molecules. A final "fixing" is then given the gas in a third chamber called the "superheater." By this time the fuel and brick-work are cooled below the optimum operating temperature. The steam and oil are shut off, and the air blast is again begun. This cycle is repeated over and over.

The value of the water gas process to the gas industry is very great. First, it permits large gas-making capacity in a small space and requires fewer men to operate. Again, it affords great flexibility in output, since water gas machines can be started and stopped as the load requires, a procedure next to impossible with a coke-oven battery. Finally, it provides a means of making gas from a cheaper fuel, oil.

Modern developments in water gas production have not changed the process fundamentally from that of Lowe, but great progress has been made in providing for completely automatic control of the machines. A water gas machine can operate now for days with no more than minor adjustments and ash removal. Modifications of the operating cycle have also been made to provide for better efficiency in fuel utilization and the production of a gas of more uniform properties.

The oil used for carburetting purposes today is much different from that used in Lowe's time. By studying the cracking properties of oils it has become possible to progress from the lighter petroleum fractions such as naphtha, gasoline, and kerosene, to heavy oils such as Bunker C fuel oil. Reduction in the cost of gas made thus decreased with the lower cost of oil used.

It is the practice in some plants to crack or "reform" natural gas or refinery still gas in water gas machines, thereby carburetting the "blue" gas with hydrocarbons. The remarkable flexibility of a water gas plant is easy to visualize from the variety of enriching materials which can be accommodated.

On the Pacific Coast, where coal is scarce and oil

Courtesy of the Consolidated Gas Electric Light and Power Company of Baltimore

A METER SETTER OF 75 YEARS AGO

abundant, a modification of the water gas process is widely used. It was developed in 1899, and the origin of the idea is claimed by two men, E. C. Jones at the Pacific Gas and Electric Company, and Leon P. Lowe, son of the originator of the water gas process. The entire apparatus for making oil gas is filled with fire-brick, arranged in a staggered pattern as in carburettors and superheaters of the conventional water gas machines. Oil is first burned with air to heat the brick. Then during the gas-making period, oil is decomposed by heat retained in the brick work. In order to gassify the lamp-black deposits which always result from the oil decomposition, steam is introduced to react with the hot carbon, as in making water gas. Gas-making periods and heating periods follow each other so that a continuous cyclic process results.

Manufactured gas supplied to consumers in this country today is frequently a mixture of gases from two

or more sources. Thermal standards set up by governing authorities require that the heating value of the gas fall within a specific range. In order to utilize all economical sources of supply and still adhere to the standards, the mixing of gases of different thermal properties is often resorted to. Natural gas, for example, may be mixed with water gas of lower heating value to obtain a mixture with a heating value between the two. In Baltimore the supply is generally a three-component mixture of coke-oven gas, carburetted water gas, and refinery oil gas, to give a mixture having a heating value of 500 B.t.u. per cubic foot. Proportions of the three gases depend on the quantities available and the load requirement.

But after gas is made, there is still much to be done before it can be used successfully in consumers' appliances. The purification of gas requires extensive chemical and physical processes, and these purification steps provide the by-products. Gas, as supplied today, must have a "purity" (if we understand by "purity" freedom from certain undesirable constituents) equal to or greater than that required of many of our C.P. chemicals. These undesirable constituents include tar, ammonia, hydrogen sulfide and organic sulfur compounds, cyanogen compounds, nitric oxide, naphthalene, and certain polymerizable unsaturated hydrocarbons. These would be odorous, dangerous to health, or give unsatisfactory service of appliances if permitted to be present in greater than minimal amounts.

Originally, little more was required or done than to remove tar and a portion of the hydrogen sulfide present. Gas flames burning mainly in streets in the open air required no more. As progress was made in lighting homes a better job had to be done. Lime for removal of hydrogen sulfide was the first purifying material used. This process was used at the Spring Gardens plant in Baltimore, and what could be more characteristic of operation in this sea-food center than that an important source of lime was calcined oyster shells?

In the latter part of the nineteenth century the use of iron oxide began to replace the lime process. This material, mixed with wood shavings, fills large steel boxes through which the gas is passed. Iron sulfide is formed by reaction with the hydrogen sulfide, and the purifying material becomes gradually used up, or spent. It is regenerated by spreading it out on the ground and exposing it to oxidation by the atmosphere. Sulfur set free by the regeneration remains in the purifying mass, and ultimately new iron oxide must replace the spent material. The spent oxide may be burned, however, to obtain sulfur dioxide for sulfuric acid manufacture.

The Seaboard process of hydrogen sulfide removal was developed and put into practice in 1921. By washing the gas with soda solution in a tall tower, hydrogen sulfide is removed as sodium hydrosulfide. The spent solution is regenerated in a separate tower by blowing air through it, either releasing the hydrogen sulfide to the atmosphere or using the fouled air in boilers. By suspending iron oxide in the wash solution, iron sulfide is formed as in the dry purifier boxes, instead of the sodium hydrosulfide. Subsequent aëration of the fouled suspension liberates solid free sulfur which can be recovered. In a modification of this process, begun in 1928, sodium arsenate solution is used, solid free sulfur being recovered from the regeneration process.

Usually, before storing the gas for distribution, it is scrubbed in packed towers or other types of washers with oil. The purpose of this treatment is to remove, by solution in the oil, naphthalene and polymerizable unsaturated hydrocarbons which may cause stoppage of service pipes if permitted to remain in the gas. Valuable light oils are recovered from the wash oil consisting largely of benzene, toluene, and xylenes, but containing also resin-forming unsaturates such as styrene and indene, which may some day become useful in the rapidly expanding field of plastics manufacture.

The best of present purification practice and distribution requirements demand that the gas be free from hydrogen sulfide, cyanogen compounds, naphthalene and ammonia to less than 0.001 per cent by volume, organically combined sulfur to less than 0.05 per cent, and nitric oxide to 0.06 part per million. The presence of suspended particles of tar fog must be practically completely eliminated, and easily polymerizable unsaturated hydrocarbons may be present in concentrations no greater than 0.02 per cent by volume.

In order to be certain that the gas meets all these requirements, constant surveillance of its characteristics must be kept through many chemical and physical tests in the laboratory. Whereas, in the early days, the consumers took what they got from the retorts, present utilization requires a "tailor-made" product. Chemical control really only began in the 1880's with determinations of the candle power of the gas. Gas analyses were limited to carbon dioxide, illuminants, oxygen, and carbon monoxide. Organic sulfur determinations began about 1905. A few years later the appearance of the Junkers flow calorimeter provided means for making determinations of the heating value of the gas. Between 1916 and 1920 the candle power standard of gas quality was replaced generally by the calorific value standard. The use of gas for lighting had by this time been superseded almost entirely by its use as a heating medium because of the popularity of the electric light. Since then control methods have been highly improved and expanded, and the adoption of several types of continuously operating, automatic, recording analytical instruments has taken place. More than a score of chemical tests are now made in the gas plant as routine procedures at frequent intervals during every day. In addition to chemical control testing, materials utilized in manufacturing and maintenance operations are analyzed, as well as by-products produced in the plant.

We shall conclude by recalling some of the many

channels through which we all come into contact with the gas industry. Gas cooks our daily bread, heats our home, and supplies heat for many industrial processes primarily. In addition, the steel industry derives coke from the manufacture of gas; coal tar and light oils supply raw materials for dyes, perfume, poison gas, paints, explosives and fertilizers, moth balls and photographic developers. Light oil and tar from water gas manufacture supply materials and swell the supply of benzene and toluene. O. E. Norman, in "The Romance of the Gas Industry" observes that, "it is chemistry that has made the gas industry so fascinating and vigorous, and is rapidly making gas the Aladdin or the ally of all industries."

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DEMONSTRATION OF THE BURNING OF A CANDLE

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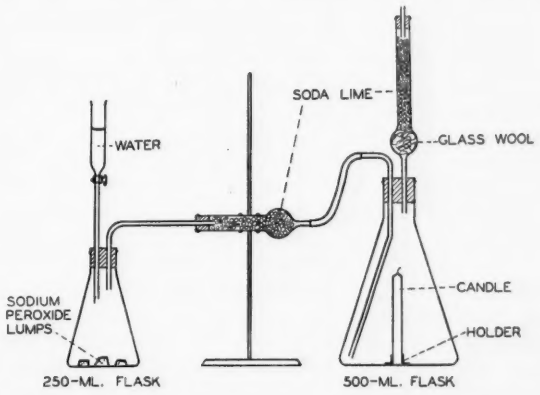
IN THE presentation of the subject of oxidation, it is customary to discuss the phlogiston theory to show wherein it failed, and then to introduce the oxidation theory of burning as developed by Lavoisier. A necessary step in doing this is to prove that the burning of *all* materials is accompanied by a gain in weight. This is easily shown for such substances as copper, iron, tin, or magnesium, but not readily demonstrated for such ordinary fuels as wood, coal, oil, or wax.

Many high-school texts illustrate an experiment to show that the gases formed by a candle when it burns weigh more than the burned part of the candle.[1] The writer has on numerous occasions attempted to carry out the experiment as illustrated with unsatisfactory results. The method involves the use of a glass chimney, filled with sticks of caustic soda, held over a burning candle. The following disadvantages of the method were noted in actual use: (1) the gain in weight is small and difficult to show convincingly with an ordinary laboratory balance; (2) often a loss in weight results due to incomplete absorption of the products; (3) the caustic soda melts and dissolves in the water produced, thus dripping down and often extinguishing the candle; (4) the experiment consumes too much time to make its use for class discussion advisable; (5) great care must be exercised that no drafts blow the gaseous products away from the absorption chimney; (6) the formation of soot complicates the usual explanation in beginning chemistry, that hydrocarbon + oxygen → water + carbon dioxide.

The writer suggests the following procedure, which he has used with very satisfactory results. An oxygen tank or generator is attached to an Erlenmeyer flask holding a candle and soda-lime tube as illustrated. The flask, candle, and soda-lime tube are weighed before the experiment on an ordinary laboratory balance. Dry oxygen is passed into the flask holding the candle. A glowing splint, thrust into the flask, ignites the candle. The flask is quickly restoppered with the soda-lime tube assembly, as illustrated. The candle burns brightly,



producing water and carbon dioxide which are almost completely absorbed in the system. When the burning ceases, the oxygen tube is disconnected, and the flask, products, and soda-lime tube are reweighed. The following are typical results:

Weight of flask, candle, and soda-lime tube before experiment	254.5 g.
Weight of flask, products, and soda-lime tube after experiment	255.5 g.
Gain in weight	1.0 g.

The advantages of this method are: (1) it yields a positive gain in weight which can easily be shown on an ordinary balance; (2) the manipulation is simple; (3) the time required is only ten minutes; (4) only water and carbon dioxide are produced; (5) the application of this method in respiration calorimeters may properly be discussed following the demonstration.

[1] MCPHERSON, HENDERSON, AND FOWLER, "Chemistry at work," Ginn and Company, Boston, 1938, p. 89; and other general chemistry textbooks.

Flower Coloration

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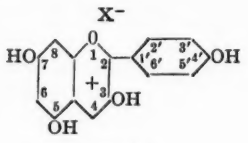
THE subject of flower coloration has been of interest to chemists and botanists for over a century, but it has been only within the past thirty years that rapid advances have been made in the chemistry and biochemistry of this fascinating subject. It is the object of this discussion to present in broad outline the main features of the organic chemistry of some of the more common types of plant pigments, and to point out recent advances in the genetic studies which may bring about a complete understanding of the biogenesis of and interrelationships between the various materials which contribute to the colors of vegetation.

The pigments responsible for the varied colors of the vegetable kingdom are, although many in actual number, representatives of only a few basic classes of organic compounds. Most of these pigments may be considered as members of two large groups: the "plastid" pigments, which occur in the plastid bodies within the plant cells, and the "sap" pigments, present in solution in the plant sap. Among the plastid pigments are included chlorophyll, the pigment of green vegetation, and a class of yellow to red pigments known as "carotenoids," pigments which are present in green leaves along with chlorophyll, in many yellow flowers and fruits, and in certain red-fleshed fruits such as the tomato and the red grapefruit.

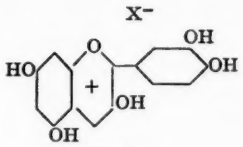
The sap pigments, while not as widely distributed in nature as the plastid pigments, represent a much larger and more varied class of substances. Interesting among these is the group of anthocyanin pigments, which are responsible for practically all of the red and blue colors of plants, flowers, and fruits. Other sap pigments are members of two main groups: the "anthoxanthins," which include the flavones and flavonols, members of which classes include many of the commonest vegetable dyestuffs, and the "anthochlors," a relatively little-known class of substances, one member of which has been shown to be a tetrahydroxy chalcone and thus to be closely related to the flavone pigments.

The colors of flowers vary over a wide range, from whites which may be due either to complete absence of all pigments or to the presence of anthoxanthin pigments of low color intensity; through yellows based upon carotenoid pigments, anthoxanthins, or anthochlors, or combinations of these; various shades of orange yellow and orange, due to anthochlors, carotenoid, or anthocyanin pigments, or mixtures of two or several of these; to reds, violets, and blues, which are based fundamentally upon the anthocyanins, the presence of certain of the other classes of pigments modifying the fundamental red or blue in a variety of ways. In this discussion will be considered those factors which govern the production and modification of colors based fundamentally upon anthocyanins. A complete consideration of the occurrence and manifestations of the other pigments so far mentioned will not be attempted; these pigments will be considered only in regard to the ways in which they affect the colors primarily due to the presence of anthocyanins.

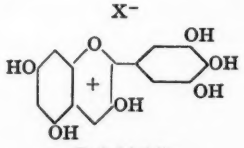
All known anthocyanins, with a few exceptions, are related to three basic substances: *pelargonidin*, derivatives of which are present in most orange red to scarlet flowers; *cyanidin*, in crimson to bluish red flowers; and *delphinidin*, the parent compound of the pigments of violet to blue flowers:



Pelargonidin



Cyanidin



Delphinidin

Peonidin is a 3′-methyl ether of cyanidin, petunidin a 3′-methyl ether of delphinidin, and malvidin (or syringidin) a 3′,5′-dimethyl ether of delphinidin.

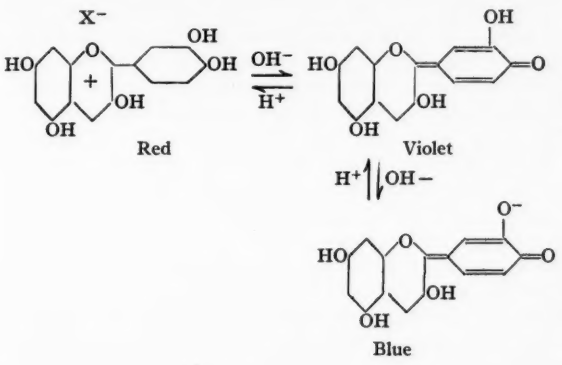
Only rarely does one of these substances (called anthocyanidins) occur as such in nature. In almost every case they occur as glycosides, sugar residues being attached at the 3- or at the 3:5-hydroxyl groups. The sugars most commonly found associated with the anthocyanidins (the anthocyanin being the glycoside) are glucose, galactose, and rhamnose. The possible number of individual pigments becomes apparent when it is considered that any of the parent types may occur as a 3-monoglycoside, a 3-bioside (two sugar residues as a disaccharide unit attached to one, the 3-, hydroxyl group), or as a 3:5-diglycoside (two sugar residues attached to the 3- and 5-hydroxyl groups).

The actual colors displayed by flowers are, however, far more varied than can be accounted for simply by considering the many combinations, which can be derived from variation in the extent of hydroxylation, methylation, or glycosidation of the fundamental pelargonidin nucleus. Modification of flower colors may be considered to involve chiefly (1) changes in "blueness" of tone, the fundamental red or blue color being preserved, and (2) dilution and background effects, in which the color is weakened or altered by

the simple "mixing" of another pigment, usually a yellow, in such a way that, for example, a flower containing a red anthocyanin may appear as salmon, orange, or brown.

Variations toward blueness may include:

(*a*) Increase in pH of the cell sap. Measurements *in vitro* on freshly crushed flowers have shown that in many cases, varieties of a single species known to contain the same anthocyanin but possessing shades differing in the degree of blueness show a difference in the pH of the cell sap, in which the bluer flower has the higher pH. Tests on pure anthocyanins in the laboratory have shown that anthocyanins and anthocyanidins are red in acid solution (the shade of red varying with the structure as will be discussed below), the color changing through violet to blue as the solution is made basic. The change in the structure of the anthocyanidin during this process has been represented as follows:



While the pH differences observed in the cell sap of living plants are not as large as those involved in the changes observed in the test tube on varying the amount of acid and base, the uniformity of agreement of blueness with higher pH in many cases indicates that even small variations in the plant play their part in the alteration of color.

(*b*) Modification of structure of the anthocyanin. In general, increased blueness of flower color follows:

1. Increased hydroxylation of the side phenyl group (pelargonidin to cyanidin to delphinidin)
2. Decreased methylation of the 3′ and 5′ hydroxyl groups (cyanidin bluer than peonidin, delphinidin bluer than malvidin)
3. Increased glycosidation (a 3:5-dimonoside bluer than a 3-monoside).

It is recognized, however, that one or more of the other factors affecting blueness may cause a complete reversal of one of these effects. An example is the case of the blue cornflower and the red rose, both of which contain cyanin (cyanidin-3:5-diglucoside).

(*c*) "Co-pigment" effects. The phenomenon of co-pigmentation was first recognized by Robinson. It is almost always a variation toward blueness and is induced by the presence of substances which are in themselves colorless or only slightly colored. The effect can be observed in crude extracts of flower petals prepared with dilute aqueous acids. The extracts of two flowers differing markedly in shade but containing the same anthocyanin will in many cases show a similar difference in shade in the cold, but on heating the extracts the bluer will change so that at temperatures near the boiling point the two solutions will show identical colors. On cooling the difference in color will return. This effect has been explained as the result of a loose combination of the co-pigment with the anthocyanin, the complex dissociating on heating and reforming on cooling.

Dilution effects are the result of decreased production of anthocyanin, the decrease usually being the result of (1) environmental effects, such as, for example, those which cause certain flowers to vary in shade from white to blue depending upon the temperature to which they are exposed; or (2) definite genetic factors, such as the common case of incomplete dominance of a gene for full color or the case of gene interaction, which reduces anthocyanin production even when the gene for full color is present. It is obvious that dilution of the anthocyanin by changes in a single genetic factor may bring about changes greater than those of simple dilution of the color due to the relatively greater effect of genetically unchanged co-pigment or background effects.

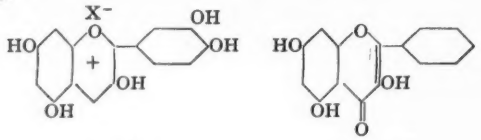
Background effects are, as the term implies, the result of simple mixing of colors as, for example, when a flower petal contains both red anthocyanin and yellow anthoxanthin or carotenoid pigment, with the result that the petals are orange in color. Background effects may be complicated by co-pigment effects when the second coloring material is a sap pigment. Combinations of anthocyanins with plastid pigments are in general examples of background effects uncomplicated by direct interaction of this sort.

The factors discussed so far cannot be considered to be the only ones affecting variations in color and shade. The deep blue of many flowers, for example delphinium, cannot be explained by any of them, the depth of blue observed being much greater than can be accounted for either by any pH which living cell sap could have or by co-pigment effects, especially since the alterations in shade produced by the latter are relatively small.

The chemistry of the anthocyanins has been thoroughly worked out, chiefly as a result of the researches of Willstätter in Germany and Robinson in England, and the structures of most of the known anthocyanins have been proved both by degradation studies and by the brilliant syntheses of Robinson and his collaborators. There remain a few representatives of this class of compounds whose structures are yet to be proved; among them is the nitrogen-containing anthocyanin betanin, the pigment of the red beet. In recent years however, the attention of chemists and biologists has turned from the problems of isolation and structure proof to the more fundamental and more complex

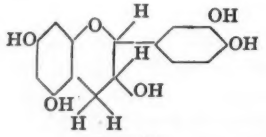
questions of biosynthesis and of the genetic relationships between the plant pigments and other products of vegetable metabolism.

One of the striking facts in connection with not only the plant pigments but with other plant components as well is the remarkable similarity in basic structure existing between different classes of compounds. A comparison of the structure of cyanidin with those of a common anthoxanthidin, quercetin, and of a commonly occurring plant material, catechin, will illustrate this:



Cyanidin

Quercetin



Catechin

This similarity in basic structure has led numerous workers in the past to postulate the interconversion of flavone derivatives and anthocyanins, the assumption in most cases being the conversion of a flavone derivative into the anthocyanin. Such transformations (for example, of quercetin into cyanidin chloride) have been carried out *in vitro*, but there is little basis for considering these results to constitute proof that similar processes occur in the plant. Indeed, the weight of evidence is to the contrary. If a flavone were converted into an anthocyanin by a simple process of reduction it would be expected that when a flavone and an anthocyanin occurred together in a flower they would be derived from the same basic structure. This is the case in some instances, but even more often it is found that the anthocyanin and the flavone occurring together are different in their basic structure, that is, in the degree of hydroxylation of the basic carbon skeleton. Magenta dahlias contain cyanidin as the anthocyanidin pigment along with apigenin, a flavone having a 4′-hydroxyl group and not the 3′,4′-dihydroxy grouping of cyanidin. It has been suggested that the flower may originally have contained two flavones, one of which was converted *completely* into anthocyanin, leaving the other, of different structure, behind.

An approach to the question, to which speculation will probably not furnish an answer, has been made on the basis of genetic studies in which the actual pigments present in a series of color varieties of known genetic constitution have been determined. Rather complete, but for the most part qualitative, studies of a number of different flowers, carried out with the aid of a group of ingenious color tests performed on dilute extracts of flower petals, have brought to light certain interesting and significant facts. In many instances the difference in amount and structure of the anthocyanins in two different color varieties of a flower has been definitely related to the appearance or loss of a specific genetic factor, or gene. Results so far obtained show that single genes can control oxidation (hydroxylation) at 3′ and 5′, methylation of the 3′- and 5′-hydroxyl groups, the substitution of a sugar residue at 5, and in some cases the pH of the cell sap. The solution of the problem of the biosynthesis of flavones and anthocyanins—whether they arise one from the other or whether they arise from a common precursor by a synthetic path which is common up to a certain point and then branches—will probably be attained by a combination of genetical studies coördinated with quantitative studies on both the nature and amount of both the anthocyanins and flavones in a series of varieties of known genetic makeup. Past studies have furnished a wide and fertile field for hypothesis, but the lack of quantitative methods expeditious enough for application to a large number of individual specimens has impeded progress toward an exact understanding of the factors which make up and modify flower coloration.

BIBLIOGRAPHY

The number of individual papers on the structures of anthocyanins is too large to permit their being given here. Some general references are:

(1) LAWRENCE AND PRICE, "The genetics and chemistry of flower color variation," *Biol. Rev. Cambridge Phil. Soc.*, **15**, 35 (1940).
(2) SCOTT-MONCRIEFF, "The biochemistry of flower color variation," from "Perspectives in biochemistry," Cambridge Univ. Press, Cambridge, England, **1938**, p. 230.
(3) ROBINSON, *J. Soc. Chem. Ind.*, **52**, 737 (1933).

A DARWINIAN SUGGESTION RIVALING MODERN SYNTHETIC CHEMISTRY

"We are engaged now in developing a scheme for growing kid gloves upon the original animal. Our old friend Darwin teaches us that you can do almost anything with breeds by judicious 'selection'; and we are convinced that, with a little care, it will be possible to produce a beast whose skin, when stripped off, will make a seamless kid glove. Our first experiments are with lizards. A lizard has four legs and a tail. Now, we believe that eventually the off fore leg can be developed into a thumb, while the other three legs and the tail can be arranged as fingers. We are crossing lizards with short tails with those with long legs; and we are now looking around for a variety of lizard with a button or two on his neck, for the purpose of breeding it in with the others, whose eyes will answer for buttonholes. The ultimate result promises to be startling. It will break up the old glove trade, and drive Jouvin to suicide. Thus it is that human ingenuity advances human civilization."

—From the very ancient files of the *Boston Courier*

The Polarographic Method of Analysis

II. Apparatus[1]

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THE polarographic method owes its name to an instrument designed by Heyrovský and Shikata, which plots current-voltage curves automatically. In 1925,[2] these authors published a photograph of the first commercially available polarograph. It consisted of a spring-driven phonograph motor, a potentiometric wheel, and a device geared to this wheel in a fixed ratio for recording galvanometer deflections. The potentiometric wheel was rotated by means of a friction drive, and thus the voltage applied to a dropping mercury electrode was increased. Simultaneously, but at a much lower rate, a sheet of photographic paper, fixed on a drum, was moved past a slit in an otherwise light-tight box. Light reflected from the mirror of a galvanometer was focused on this photographic paper. Changes in current obtained during the change in voltage would then deflect the galvanometer and be recorded as a curve with the voltage as abscissa and the current as ordinate. This rather crude device sold for about fifty dollars, exclusive of the galvanometer.

The development of the polarographic method made greater accuracy of this instrument essential and numerous refinements in its design and construction have been made, with the result that the polarograph of today can rank with the finest pieces of scientific equipment. Unfortunately, these developments caused such a big increase in price that many laboratories were unwilling to acquire an instrument on the chance that it would be suitable for their particular problems. However, in the past few years interest in polarography has grown, for American instrument makers began to manufacture polarographs[3] and to coöperate with industry in developing applications of the method. Yet, for small laboratories and student instruction, the acquisition of polarographs is still out of the question and a less complicated mechanism is desirable.

It is the purpose of these papers to emphasize that the principles of the polarographic method can be taught and many applications be carried out with the simplest of instruments. To be satisfactory, we must have equipment which permits us to apply known voltages to a cell consisting of one large non-polarizable and one small easily polarizable electrode and to observe the current which flows at that voltage. The automatic recording feature is not necessary, since the curves can be plotted on graph paper as Heyrovský did years before his invention of the polarograph. One such device which gives satisfactory results has been built in this laboratory for less than ten dollars and is used in combination with a forty-dollar galvanometer. Many of its parts are undoubtedly kept in stock in student laboratories. It will be described in detail and its applicability will be demonstrated by some examples in this and subsequent papers.

[1] For Part I and general references see J. CHEM. EDUC., 18, 65 (1941).

[2] *Rec. trav. chim.*, 44, 498 (1925).

[3] In the United States at least five firms are constructing polarographs or similar equipment for use with the dropping mercury electrode which are sold under various trade names.

ESSENTIAL EQUIPMENT

The parts of this apparatus were purposely chosen on the basis of cheapness, which necessarily cuts down the accuracy of the results obtained. At a relatively little higher cost, more precise resistors and voltmeters can be substituted and the setup made accurate enough for most analyses. Figure 1 is a reproduction of this simplified setup in which all hidden connections, wiring, and resistances have been made visible by drawing them on the mounting board. This figure becomes clear upon examination of Figure 2, which shows the wiring diagram schematically. The apparatus consists of four units: (1) the source of electromotive force (E.M.F.), (2) the polarizing unit, (3) the cell, and (4) the galvanometer.

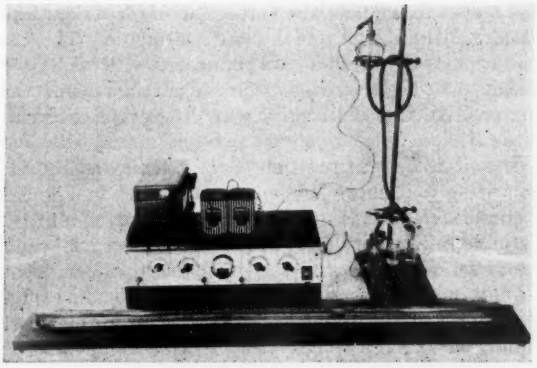

FIGURE 1.—APPARATUS FOR OBTAINING POLAROGRAMS MANUALLY

Source of E.M.F.—A 4- or 6-volt storage battery B is best, but two or three normal dry cells in series can also be used.

Polarizing Unit.—In Figure 2, two types of polarizing units are shown, either of which can be used by manipulating the double-pole, double-throw switch T_1. When switch T_1 is in position a the *normal* polarizing unit is connected. It consists of a voltmeter V, slidewire R_1

with tap key T_2, and additional resistance R_2. The voltmeter V is connected across the ends of the slidewire R_1 and indicates the drop in potential across this wire. The most inexpensive 3- or 5-volt voltmeter obtainable will be satisfactory; rarely more than two fixed settings are of interest and a previous calibration will insure a fair accuracy. The slidewire R_1 was constructed in this laboratory from a meter stick and a No. 29 nichrome wire (with a resistance of 5.28 ohms per foot).

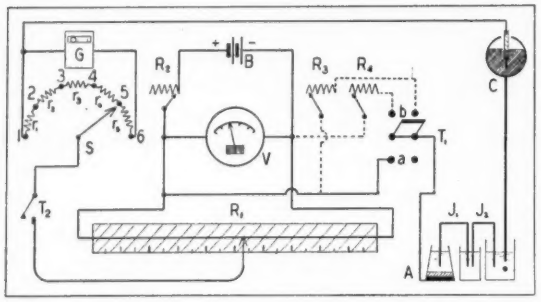

FIGURE 2.—CIRCUIT OF APPARATUS SHOWN IN FIGURE 1. FOR EXPLANATION SEE TEXT

The sliding contact was made of a strong spring supported by a brass arm. After the wire had been cleaned with gasoline and subsequently greased with a trace of vaseline, good contact was insured all along the wire. Commercial wheatstone bridges can be bought for as little as five dollars. For student use, a simple tap key T_2 seems advisable as a protection for the galvanometer. For research work, a switch will be found more advantageous. R_2 is a variable resistance of 100 ohms and serves to regulate the voltage across R_1 taken from battery B and indicated by the voltmeter. The two center posts of switch T_1 are connected with each other and lead to the reference electrode A, thus connecting the positive side of the slidewire R_1 to reference electrode A.

If switch T_1 is in position b, the *anodic and cathodic* polarizing unit shown by interrupted lines in Figure 2 is connected. It adds to the *normal* polarizing unit two variable resistances R_3 and R_4, of 20 ohms each, which are in series. They are placed parallel to the slidewire R_1 and have a connection between them leading off to the reference electrode A. If R_3 and R_4 are perfectly equal, the voltage applied from R_1 to the cell is zero if the slide makes contact at the 50-cm. mark; above 50 cm. the dropping mercury is negatively polarized, below 50 cm. it is positively polarized. Thus, without interruption, a decreasing anodic polarization is followed by an increasing cathodic polarization. This feature is of real significance only when the automatic recording devices are used; it is included here for purposes of instruction. A polarity-changing switch between the *normal* polarizing unit and the electrolysis cell may be found more convenient.

The Cell.—The electrolysis cell sketched in Figure 2 consists of two half-cells, the polarizable dropping mercury electrode C and the non-polarizable reference electrode A, connected by suitable bridges J_1 and J_2.

The dropping mercury electrode C has many advantages as a polarizable electrode for polarographic analyses, as has been shown in the preceding paper.[1] It consists of a leveling bulb serving as a mercury reservoir, which is connected to a fine capillary by means of thick-walled rubber tubing, 60–70 cm. long, which has been thoroughly cleaned and dried. This type of electrode was designed by Kučera and has been used by Heyrovský and collaborators in the development of the polarographic method. A number of modifications have been suggested; they may be advisable for the most accurate work but cannot surpass the Kučera type for simplicity and flexibility and will not be described here. The capillary is constructed by pulling out glass capillary tubing of 0.5-mm. internal diameter. A fairly thick tip with a round hole, 20–30 μ in diameter, will be obtained when the capillary is cut to its proper length if sufficient glass is accumulated before the tubing is pulled out. A red line in Jena glass makes it possible for an amateur to do this without twisting the glass, so that a straight bore with a round hole results. However, there are also on the market several brands of capillary tubing with a bore of 50 μ whose use has become more prevalent in recent years. The Corning Glass Works manufacture such tubing as "marine barometer tubing"; it may be found to be slightly larger in diameter than claimed, but lengthening of the capillary will reduce the dropping rate of the mercury to the desired point.

In the construction and use of the dropping mercury electrode, a few words of caution are in order. First of all, the capillaries, whether obtained commercially or prepared in the laboratory, must have their ends covered at all times to prevent any dust from entering. After they have been connected with the rubber tubing and filled with mercury, they should be kept immersed in *distilled* water until used. After the experiment, the capillaries *while dropping* should be washed with distilled water, cleaned off with filter paper, and reimmersed in distilled water. Only then should the flow of mercury be stopped by lowering the mercury reservoir. Careful observation will show that the water is sucked up about $^1/_2$ cm. into the capillary. During the actual experiment, similarly, some of the solution is sucked up each time a ripe drop has fallen. Keeping the tip of the electrode in distilled water when stopping the flow of mercury will keep it washed out and the capillary will remain in working order for many years, as has been found by actual experience. Some experimenters recommend lowering the tip into a pool of mercury at the end of an experiment, but such capillaries do become unsatisfactory at times and have to be cleaned out with *aqua regia*. A satisfactory electrode will drop at the rate of 6–8 seconds per drop in distilled water (or 3–4 seconds in 0.1 N potassium chloride) if the mercury pressure is about 60 cm. This pressure should be measured between the tip of the capillary and the level of the mercury in the reservoir or leveling

bulb. It is well to find the drop rates at several pressures of the mercury and also to find at what pressure the flow of mercury through the capillary will cease.

Only the purest mercury should be used for the electrode, and contact between the mercury and wires of the apparatus must be made by means of platinum wires to prevent any amalgamation. The mercury can be purified by treatment with some oxidizing agent or by bubbling air through the mercury after it has been covered with a layer of water. This should be followed by distillation in a stream of air (under the hood!) and finally, by distillation in vacuum. In all work with mercury the utmost care should be taken that none of it is spilled on the desks or floor in the laboratory; furthermore, the rooms should be frequently aired to prevent poisoning. A simple precaution in polarographic work is to have a large tray of water beneath the electrode stand so that any spilled mercury will immediately be covered with water. If the glass capillary is in a fixed position and all the reagents and solutions are moved onto it, such a tray provides valuable protection against mercury poisoning.

The electrolysis vessels vary in size and shape depending on the particular study. The analyses are simplest if carried out with 5–10 cc. of solution. Microanalyses of single drops are possible but special vessels are necessary. Ordinary beakers suffice for work in which oxygen does not interfere. Often, however, it is necessary to remove the dissolved oxygen and carry out the analysis in the absence of air. In this case small bottles can be used, closed off by means of a rubber stopper through which is passed a gas inlet tube reaching to the bottom of the bottle and a gas outlet tube leading to a trap.

In early work with the polarograph, small vessels of the shape of Erlenmeyer flasks were found desirable, because the mercury in the bottom of the electrolysis vessel was used as the reference electrode and its surface had to be large to make it non-polarizable. It was necessary to measure its potential against a standard calomel half-cell. The use of a large saturated calomel half-cell as a non-polarizable reference electrode has become more prevalent in the last five years because it simplifies the procedure and permits the direct comparison of all records obtained under similar conditions. It has one disadvantage, nevertheless, since one or two agar bridges become essential; these increase the resistance in the circuit and will alter it from time to time as different bridges are used. The use of two agar bridges J_1 and J_2 together with a junction vessel, as shown in Figure 2, is advisable. If the reference electrode A is a saturated calomel half-cell, the first agar bridge J_1 should be also saturated with potassium chloride to prevent its contamination. The junction vessel similarly contains saturated potassium chloride which should be renewed frequently. The second agar bridge J_2 may then be filled with the same solution as that in the cell or may be saturated with potassium nitrate, which is indifferent to most reactions studied. The preparation of a saturated calomel half-cell is familiar to every student of physical chemistry. Suitable bridges can be formed from a three per cent solution of agar saturated with the necessary salt.

The Galvanometer.—Most desirable for polarographic work is a very sensitive galvanometer with low internal resistance and a long period of swing. The instrument G described here does not meet these requirements fully, but is nevertheless desirable because of its ruggedness and low cost, which are combined with a relatively high sensitivity. It is a Leeds and Northrop type with inclosed lamp and scale, a period of 3 seconds, an internal resistance of 1000 ohms, and a maximal sensitivity of at least 2.5×10^{-8} A./mm. Its critical damping resistance is 15,000 ohms. This means that in order to make the galvanometer indicate the flow of current in as short a time as possible for the type used, without overshooting its mark, an external resistance of 15,000 ohms, S, must be shunted across its terminals.

Critical damping is of greatest importance in polarographic work, because, contrary to most other electrochemical work, the galvanometer is not used as a null-point instrument but is used to measure currents. Furthermore, these currents are never constant, varying from practically zero to some finite value with the growth of each drop of mercury once every few seconds. The effect of the external damping resistance may be visualized by remembering that a galvanometer, deflected from its zero position, will generate electricity in its coil while it is moving in the stationary magnetic field on its return to the zero position. A critical resistance can then be found which, when placed across the terminals of the galvanometer, will slow down the movement of the coil just enough so that it will reach its zero position without overshooting.

The necessary shunt S was constructed from a gang switch and fixed resistors r_1–r_5 of 2, 25, 250, 2500, and 12,500 ohms in series. In this way the galvanometer can be used at five different sensitivities. The total resistance is slightly in excess of 15,000 ohms but the resulting overdamping is insignificant.

MANIPULATION

In setting up this equipment care should be taken that all contacts are firmly connected, soldered where possible. The slidewire should make perfect contact over its entire length. To test for satisfactory conditions, have switch T_1 in position a, place a fixed resistor of about 5 megohms across the cell terminals instead of the cell, press down the key T_2 and observe the deflections of the galvanometer while the sliding contact is moved along the slidewire. A steady increase in the deflection of the galvanometer to the right should result. If an accurate resistor is used and the sensitivity of the galvanometer has been previously determined, the cheap voltmeter can be easily calibrated. For instance, in the present case it had to be set at 2.1 volts in order to have a potential drop of 2.0 volts across the slidewire. At this setting each millimeter corresponded to 2 millivolts, increasing from left to right along the slidewire. Naturally, the voltmeter can be calibrated

for other values in a similar way. Next, using Ohm's law for all calculations, the galvanometer sensitivities corresponding to different settings of the shunt should be determined. At position No. 6 in the above shunt the galvanometer is used at full sensitivity and one millimeter on its glass scale corresponds to 2.25×10^{-8} A. At other positions of the shunt the following galvanometer sensitivities were found:

Position No. 5	1.25×10^{-7} A./mm.
Position No. 4	1.24×10^{-6} A./mm.
Position No. 3	1.30×10^{-5} A./mm.
Position No. 2	1.70×10^{-4} A./mm.
Position No. 1	Zero

If the apparatus is used for more than student instruction it will be worth while to extend the scale of the galvanometer by removal of the furnished glass scale and substitution of a large millimeter scale at a greater distance. An additional lens may be necessary but the distance can be so chosen that one millimeter on this new scale corresponds to 0.01 microampere. After these preliminary tests check the saturated calomel half-cell, agar bridge, and the dropping mercury electrode by connecting them into the circuit.

A suitable solution for this check is 25 cc. of 0.1 *N* potassium chloride open to the air, to which 5 drops of 0.1 per cent methyl red have been added, for reasons to be described in a subsequent paper. The customary procedure is to introduce the capillary through a stopper into the vessel containing the solution; careful study in this laboratory has shown, however, that slight changes in the slant of the tip of the capillary produce measurable errors. It was found more advisable, therefore, to fix the capillary tightly in place on a firm stand and move the electrolysis vessel onto the capillary. The sliding contact is then placed at 0.1 volt, the tap key held down, and the galvanometer

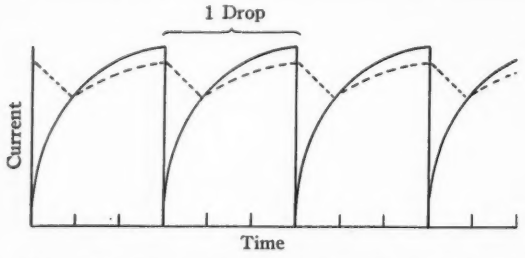

FIGURE 3.—SCHEMATIC REPRESENTATION OF CURRENT CHANGES DURING THE GROWTH OF THE MERCURY DROPS OBTAINED WITH A VERY FAST GALVANOMETER (CONTINUOUS LINE) AND WITH A SLOW GALVANOMETER (INTERRUPTED LINE)

sensitivity changed by means of the shunt to such a value that the deflections of the galvanometer may be easily measured. Notice that after the first few oscillations the galvanometer deflections reach the same maximum at regular intervals just before the drops fall off. With a very fast galvanometer the current can be followed during the growth of a single drop: it starts from practically zero and rises abruptly when the drops first form; as the drops approach their maximal size the change of current becomes smaller (Figure 3, continuous line). A slow galvanometer cannot follow these changes as well and thus smoothes out the oscillations (see the interrupted line in Figure 3). In the automatic plotting of the current–voltage curves with the polarograph many investigators measure the mean current observed during the oscillations. In the above setup, however, it is best to read the maximum deflections. Even when the oscillations are fast, their peak can be found accurately by moving a strip of paper up to the edge of the deflections. Since the method is only relative it makes little difference what fraction of the actual current is measured as long as the operator remains consistent throughout. At this point it is well to emphasize the importance of a vibrationless stand for the dropping mercury electrode as well as for the galvanometer. *Unless the drops fall under their own weight when they are ripe, no reproducible results can be obtained and the method becomes useless.* Neglect of this precaution had caused much distrust in the method in several laboratories where it is held in high esteem today.

We are now ready to prepare a current–voltage curve. This is obtained by observing the galvanometer deflections at a large number of different applied voltages, for instance at intervals of ten millivolts over the range of E.M.F. from zero to 2 volts. If we plot the observed current against the applied voltage we obtain a typical polarogram.[1] We see that the current starts from practically zero, increases rapidly up to 0.2 volt, and then reaches a short plateau. A second increase in current at about 0.7–1.2 volts and a second plateau is finally followed by a third increase in current near 2.0 volts, which would reach no limit if the voltage were further increased. Every increase in current followed by a plateau is S-shaped; it is called a wave or step. We can measure the height of this wave and the potential at the midpoint of this wave, which in most cases is its inflection point. These two quantities, wave height and half-wave potential, make a quantitive and qualitative analysis possible in polarography. The first plateau on the polarogram obtained represents the reduction of oxygen to hydrogen peroxide. The second plateau represents an additional reduction of the hydrogen peroxide to hydroxyl ion. The final increase is due to the reduction of the potassium ion. Details of the analyses of such curves will be described in the next paper.

Next, a polarogram of this same solution should be obtained after the oxygen has been removed by a stream of oxygen-free gas. Tank hydrogen or nitrogen is simplest to use; naturally also hydrogen prepared in the laboratory by electrical or chemical means is satisfactory, provided it is freed of impurities by being led through suitable washing solutions. Depending on the volume of the solution and the shape of the vessel, it will take from five to twenty minutes to remove all the oxygen which might produce a measurable current in this setup. The above procedure is then repeated

and a curve is obtained in which the waves due to the oxygen reduction are absent and the final increase due to the reduction of the potassium ions remains. Of course the flow of gas through the solution must be stopped before any current is measured because, as stated before, the drops of mercury have to fall under their own weight and should never be forced off by motion in the solution.

Finally, the "anodic and cathodic polarization" should be tested by throwing the double-pole, double-throw switch to position *b*. Place a fixed resistance of about 10,000 ohms across the cell terminals, set the sliding contact at 50 cm., adjust resistance R_3 almost to its full value, and fix resistance R_4 in approximately the same position. Then press the tap key and, observing the galvanometer deflections at a high sensitivity, adjust R_3 and R_4 until they are absolutely equal, which is indicated by a zero reading of the galvanometer. After this operation again connect the cell and repeat the curve obtained before with 0.1 *N* potassium chloride, starting from zero applied voltage which is now at the 50-cm. mark. If the potential drop across the slidewire is adjusted to 4 volts, each millimeter will correspond to 4 millivolts, so that the same curve should result as above during cathodic polarization, *i. e.*, if the sliding contact is moved to the right. If it is moved to the left from the 50-cm. mark a new portion will be added to the curve which is due to anodic polarization of the dropping mercury electrode. It will be noted that in this anodic polarization a marked galvanometer deflection to negative values occurs. This represents the anodic oxidation of mercury to mercurous ions, which immediately combine with the chloride ions present in the solution to form mercurous chloride. The point to remember from this curve is that any deflection of the galvanometer to the left, or to negative values, represents an oxidation at the dropping mercury electrode while any deflection to the right of its zero position represents a reduction at the dropping mercury electrode.

RESISTANCE IN THE CIRCUIT

As will be shown in later papers, the resistance of the circuit is of great importance for the calculation and interpretation of the results. It is not necessary to know this resistance more accurately than to a few hundred ohms, and changes less than 500 ohms in the above setup may be neglected. This eliminates resistances R_1, R_2, R_3, and R_4 from our consideration. The resistance of about 50 ohms in the capillary itself is similarly insignificant, but not the resistance in the solution, which can amount to several hundred or a thousand ohms when no bridge is used and a large layer of mercury at the bottom of the vessel is made the anode. When agar bridges are used, large resistances are introduced which can vary from 2000 to 5000 ohms and have to be measured. Of the numerous methods which are available for these measurements in polarographic work only the simplest one will be mentioned here. A large enough voltage is applied to the cell so that the voltage lost by polarization of the electrode can be neglected; the resulting current is measured. If different voltages are applied from a *B* battery to the cell and the corresponding current is measured with the galvanometer at its lowest sensitivity, the resistance calculated on the basis of Ohm's law approaches a limit as the applied voltage increases past 9 or 10 volts. The value thus obtained may then be used in further calculations as the resistance of the cell.

In the commercial polarograph, the galvanometer resistance can usually be neglected in such calculations. However, in the apparatus described here this is not the case. The internal resistance of the galvanometer is 1000 ohms and that of the shunt 15,000 ohms. From this we can calculate that the resistance introduced in the circuit varies from about 1000 ohms at position No. 6, increases to 2100 ohms at position No. 5, drops to 250 ohms at position No. 4, and reaches a minimum of 2 ohms at position No. 2. These values will have to be added to the resistance of the cell for the correction of applied potential, as will be shown later.

THOMAS MARTIN LOWRY

(Frontispiece)

BORN at Low Moor, Bradford, Yorks, England, in October, 1874, Thomas Martin Lowry was the second son of Reverend Edward P. Lowry. He received his education at Kingswood School, Bath and Central Technical College, South Kensington, receiving the degrees of D.Sc. (London) in 1899; F.R.S., 1914; O.B.E., 1918; C.B.E., 1920. His first position was that of assistant to Professor Armstrong at the Kingswood School, from 1896–1913. After his marriage to Eliza Wood, the daughter of a minister, in 1904, Lowry also carried on work as lecturer on chemistry at Westminster Training College from 1904–13. From there he went to Guy's Hospital Medical School, where he had a post from 1913–20. From then on until his death in 1936, Professor Lowry held the position of Professor of Physical Chemistry at Cambridge University. He specialized in the studies of rotatory polarization, photosynthesis, and allied fields. His published books include "Historical Introduction to Chemistry," "Inorganic Chemistry," and "Classbook of Physical Chemistry."

Dr. Lowry held many positions during his lifetime. A member of the Council of the Chemical Society from 1912–16, he was Vice President from 1922–4. He was Vice President of the Faraday Society twice, from 1913–18, and again from 1927–8; he was then elected President in the latter year. Dr. Lowry was vice president of the Oil and Color Chemists Association from 1925–8. He served his country during the first World War and after; he was Director of Shell Filling from October, 1915, to June, 1919; an associate member of the Ordnance Committee from 1917–19; and an Additional Member of the Chemical Warfare Committee from 1918–25. He was an Officer of the Order of St. Maurice and St. Lazarus in 1919.

A History of the Match Industry

M. F. CRASS, JR. *Washington, D. C.*

PART I—CHEMICAL FIRE MAKING PRIOR TO INVENTION OF THE FRICTION MATCH

Discovery of Phosphorus

IT WAS the discovery of the first non-metallic element, phosphorus, by Hennig Brandt[1] in the year 1669 that first enabled civilized man to establish fire by other than purely mechanical means. Brandt, a merchant of Hamburg and a patient and persevering alchemist in his spare time, spent many weary nights boiling urine with the hope of eventually obtaining a solvent or essence that would transmute silver into gold. His astonishment must have been great, therefore, when upon examining some retort residues following the boiling of a hogshead or two of his filthy liquid, he discovered a small amount of waxy material which, when subjected to the slightest warmth or friction, vigorously took fire (*1*). Brandt had accidently succeeded in isolating phosphorus from some of its combinations, and he lost no time in displaying the amazing material to his friends.

Krafft of Dresden, hearing of Brandt's discovery from Johann Kunckel, straightway journeyed to Hamburg and offered to purchase the secret, on the condition that no one else be told of the method of preparation. A bargain was struck between the two men for a consideration of $200, and Krafft departed with the secret, refusing to take Kunckel into his confidence. The latter thereupon resolved to discover the secret for himself and after a great deal of experimentation was finally successful in 1672.

The exact nature of the element was not understood, but the fact that it was so flammable that a minute portion of it, rubbed between two pieces of paper, took fire, was so wonderful that for several years it caused excitement all over Europe. It was necessary to manipulate nearly two hogsheads of urine in order to obtain a single ounce of phosphorus, hence the substance was sold to the curious in minute quantities at enormous prices. In 1674 the Swedish chemists Scheele and Gahn discovered the element in bones, and developed a process that enabled the recovery of larger amounts more reasonably. In 1680 Godfrey Hankwits began the manufacture of phosphorus in London. After making a few ounces, Hankwits would start out on his travels over England, selling his stock at the rate of 50 guineas the ounce. In the same year, Robert Boyle applied a small amount of the element between folds of coarse paper and ignited a splint tipped with sulfur in the resulting flame (*3*).

Because of the difficulties involved in its preparation, resulting in prohibitive cost, interest in phosphorus subsided after its spectacular introduction and the element remained for over a century without special attention, until the introduction of friction matches created an industrial demand for it. It is worthy of note that for 50 years prior to the use of phosphorus in friction matches, a determined effort had been made by countless experimenters to find an effective substitute for the tinder box, and a large number of fire-making contrivances based upon chemical principles had been introduced. One of the simplest methods of obtaining fire, however, that of the ignition of phosphorus by means of friction, was strangely overlooked during this period.

Phosphoric Taper

Between the years 1780 and 1830 a great variety of chemical fire-making contrivances made their appearance. Many of these devices have been preserved and are on display in museums, the most notable and complete collection being that of Bryant and May in London. These early contrivances of chemical nature were intermediary between mechanical methods and friction matches, and finally led to the introduction and development of the first true friction match. Probably the earliest of the chemical fire-making contrivances was the *phosphoric taper*, also called *phosphoric candle* and *ethereal match*, introduced in France in 1781 (*4*). This device consisted of a 4-inch glass tube, in the bottom of which was placed a small piece of phosphorus. A thin waxed taper with frayed end was inserted in the tube, the latter then being hermetically sealed and a circle drawn around it with a glazier's diamond at the end furthest from the phosphorus. Dipping the tube into warm water, to melt the phosphorus and make it adhere to the frayed end of the taper, prepared it for use. When a light was desired the tube was broken at the circle with the aid of the teeth or otherwise, and the taper withdrawn, to burst into flame upon contacting the outer air.

Phosphorus Box

This device, also referred to as the *portable phosphorus box*, *phosphorus bottle*, and *pocket luminary*, was a further development of the phosphoric taper, making its first appearance in Italy in 1786, and rapidly spread-

[1] Credit is given Brandt for the discovery of phosphorus for the reason that scientific knowledge concerning its properties dates from his isolation of the element. That evidence exists as to its preparation well over 100 years prior to Brandt's time is shown by the following recipe (*2*) taken from the works of Paracelsus:

"Take urine and thoroughly distil it. Water, air, and earth will ascend together, but the fire remains at the bottom. Afterwards mix all together and distil again four times after this manner; and at the fourth distillation the water will ascend first, then the air and the fire, but the earth remains at the bottom. Then receive the air and the fire in a separate vessel which put in a cold place, and there will be congealed certain icicles, which are the element of fire. This congelation will take place during distillation, but the solidification is much more ready when cold."

ing to Paris and London (*4*). The outfit consisted of a small bottle containing phosphorus which had previously been momentarily ignited so as to coat the inside walls with a thin film of oxide, and a small number of wooden splints tipped with sulfur, all contained within a small metal box. Introduction of one of the splints into the bottle so as to cause some of the partially oxidized phosphorus to adhere to the sulfured tip, followed by withdrawal of the splint from the bottle, generally resulted in ignition. If the splint failed to ignite spontaneously it was rubbed on the cork of the bottle in order to make it take fire.

An effort to stabilize the phosphorus and make the operation a safer one for the uninitiated resulted in what was apparently the first friction match composition. This composition, introduced by de la Tour in 1805 and consisting generally of phosphorus, wax, and oil, was used in the bottle in place of the partially oxidized phosphorus. The sulfured splints, after being dipped into the bottle, were ignited by rubbing on the bottle cork.

Other efforts were made to improve this method by reducing the flammability of the phosphorus. In 1809 a French patent was granted for "a peculiar composition of phosphorus match lights." This was an effort to make the phosphorus more manageable by mixing eight parts of "half-melted" phosphorus with four parts of magnesia. Tubes were also introduced containing equal parts of phosphorus and sulfur carefully fused together into which untipped splints were introduced. Ignition of the splints was then accomplished by means of friction.

Pyrophorus

Next came what was called the *pyrophorus* or *pyrophosphorus*, consisting of a sealed glass tube containing a finely divided pyrophoric powder free from phosphorus, which ignited spontaneously when the tube was broken open and the contents scattered. According to Clayton (*5*), Homburg's pyrophorus consisted of a roasted mixture of alum, flour, and sugar, hermetically sealed in a glass tube. Hare's pyrophorus (1831) was made by heating prussian blue to redness in a glass tube, which was immediately afterward sealed.

A number of United States patents were granted for pyrophoric mixtures, particularly between the years 1860 and 1870, although there is no evidence that would indicate wide or even successful application. One of the latter mixtures consisted of finely divided potash, charcoal, alum, and rye flour, which had been heated to redness for 40 minutes in a hermetically sealed iron cylinder, after which the material was pulverized and packed in small airtight vessels (*6*). The inventor claimed that by placing a small amount of the powder in the bowl of a pipe and applying suction through the mouthpiece, the powder would take fire and ignite the tobacco in the pipe bowl.

An application of the pyrophoric principle to modern fire making was patented (*7*) as recently as 1937, the patent covering "a safety ignition mixture, ignitable by friction," consisting of a mixture of substances yielding oxygen; semipyrophoric metals from Group IV of the periodic table, abrasives, and a binding material. The pyrophoric metals (iron, nickel, or cobalt) were prepared by heating the metallic oxalate to 400°C. in a stream of dry hydrogen.

Instantaneous Light Box

By far the most useful and practicable chemical fire-making appliance prior to the introduction of the friction match was the so-called *instantaneous light box*, invented in France by Chancel shortly after 1805, and widely used for a period of over 40 years in both Europe and the United States (*8*). This appliance consisted of a small metal box containing a well-stoppered bottle of sulfuric acid, and a number of wooden splints tipped with a composition containing potassium chlorate, sugar, and binding material, the latter generally being a vegetable gum such as arabic or acacia. When dipped in the acid and withdrawn, the splints would take fire. The principle involved, that of oxidation by chlorates in the presence of strong sulfuric acid, had been previously discovered by the pioneer French industrial chemist, Berthollet.

Professor H. Dussance of the Polytechnic Institute of Paris describes an improvement of this method as follows (*9*):

> "Inflammability became easier when the end of each sulphureted match was provided with a paste called 'oxygenated,' formed of powdered sulphur 25, chlorate of potassium 30, lycopodium 2, cinnabar 1½, agglomerated by 5 or 6 parts of solution containing 4 of gum arabic and 3 of tragacanth. This mixture, once dried, could be effectively inflamed when the match tip was put into contact with asbestos saturated with concentrated sulphuric acid. This acid decomposes the chlorate of potassium, sets free the chloric acid which is immediately decomposed and produces nascent oxygen, which burns the combustible substances."

Because of the many instances of acid leakage whereby clothing, upholstery, and rugs were destroyed, it became common practice to insert finely fibered asbestos into the bottle in order to absorb the acid, as described above.

According to an early report (*8*), it was not always possible to get a brilliant flame with instantaneous light box splints. The report follows:

> "Instead of a brilliant flame, the match smouldered only and spurted acid about to the detriment of clothes and a peaceful disposition. As a stroke of economy, such a wetted match was often put back with the other splints for further use in the future, but on contacting one that was more energetic, ignited it, and thus the entire collection was lighted at once and shot out in all directions."

In spite of such objections, the appliance was extensively used, particularly by the wealthier classes in the larger urban centers. It appears that one of the principal objections to use of the tinder box was the possibility of "knuckle skinning," especially when a light was struck in the darkness. That such complaint was common enough is shown by the following advertisement that appeared at this time (*3*):

> "Save your knuckle, time, and trouble; use Heurtner's Empyrion, price one shilling."

The term *Empyrion* was often used for the instantaneous light box. Other names in common use were *Chemical Matches*, and *Oxymuriated Matches*.

Developments and modifications of the original principle were many, in spite of the disadvantages encountered, which usually consisted of weakening of the acid because of moisture absorption, spilling or spurting of the acid, accidental ignition of the entire splint supply, and lack of uniformity in the type of flame produced. A box of fifty "matches," together with a phial of sulfuric acid, is reported (*1*) as costing about two dollars in the United States during its period of popularity. An interesting modification patented (*4*) in England in 1824 enabled a person lying in bed or otherwise at ease to obtain a light simply by pulling a string. This contrivance was enclosed in a thin iron box with deep hinged lid. The string passed over a pulley in such a way as to remove a long glass stopper from an acid bottle, bringing it into contact with a compounded splint, which would then ignite. A further tug on the string changed the position of the burning splint in such a way as to ignite a small spirit lamp with which the box was equipped.

A further modification was the *Promethean Match*, patented in England in 1828 by Samuel Jones and consisting of a small glass capsule, hermetically sealed, containing sulfuric acid. The outside of the capsule was coated with a composition containing potassium chlorate, sugar, and binding material, the prepared capsule being compactly wrapped up in a roll of paper about three inches long. When the glass was broken with the teeth or with the aid of a pair of pliers (sometimes furnished as a part of the outfit) the chlorate would ignite, firing the paper. Because of the high cost of this "match" and the disastrous results often caused by promiscuous disposal of the acid-soaked remnants, it did not come into extensive use. Jones used the following coating formula: sulfur 24.7, lycopodium 8.8, potassium chlorate 34.9, and gum 31.4. The acid consisted of 61.9 per cent H_2SO_4 and 38.1 per cent water, with a trace of indigo to give the liquid a pleasing and perhaps mysterious appearance.

Electropneumatic Lamp

Many varieties of the *electropneumatic lamp* or *electropneumatic fire producer* were invented between 1775 and 1830, the principle involved being the ignition of a fine jet of hydrogen gas by means of a spark from a piece of charged rosin. The famed German chemist Döbereiner invented in 1823 what is perhaps the best-known portable device of this nature. Hydrogen gas was generated by the action of dilute sulfuric acid upon zinc. The gas was then directed in a thin stream upon platinum sponge in contact with the air, a jet of flame resulting which burned as long as the supply of hydrogen lasted or until it was shut off. An interesting example contained in the Bryant and May Museum consists of a cylinder of frosted glass containing the gas generator, mounted on a square, wooden stand. On top of the glass cylinder is a midget in vivid costume of green, red, and gold, smoking a large cigar which forms the end of the gas nozzle, and holding a hinged glass cover for the small compartment containing the platinum.

It must be emphasized that the various types of chemical fire-making contrivances already described were considered more or less as luxuries and were used principally by the wealthier classes living in towns and cities. Folk living in outlying districts and the great bulk of the middle and lower classes still depended upon the tinder box as their primary source of fire, and it was not until well after the introduction of the phosphorus friction match that both the tinder box and the instantaneous light box became really obsolete. An American author in 1877 wrote as follows (*10*).

"Fifty years ago the tinder box was as indispensable to the household as the well-filled match safe of today."

Another account, written by O. C. Barber in 1850, shows that even at this comparatively late date, matches were not available to all sections of the population:

"Method of distribution of matches in the early fifties was by canal or wagon, at least in the west. In Ohio and west of Ohio the railroads then running would not transport matches, which they considered as being too dangerous. It was only in the early sixties that railroads began to carry matches. The writer has been in every Ohio county with a horse and wagon, also in Michigan, Indiana, and West Virginia, selling small lots of goods (matches) to merchants."

PART II—FRICTION LIGHTS OR LUCIFERS

The culmination of the various contraptions and contrivances of chemical nature into a match intentionally designed to take fire from friction of prepared ingredients upon an ordinary surface finally took place in England in the year 1826, when John Walker, an apothecary and chemist of Stockton-on-Tees, Durham County, prepared and sold his *Friction Lights*. Although friction matches were undoubtedly made prior to this time, there is no record of such matches having been prepared, sold, and successfully used by the public. Born in 1781, Walker became a surgeon's apprentice at a rather early age and, during his apprenticeship, conducted many chemical experiments which gave him considerable local status as a scientist. Being of a studious and retiring nature and not caring for the sometimes revolting duties required of a surgeon in those early days, Walker abandoned the profession of surgery and went to work for a firm of druggists. In 1819 at the age of thirty-eight, he established himself as a pharmacist in Stockton, remaining in this business until a few years prior to his death in 1857 (*11*).

Walker's first recorded sale occurred on April 7, 1827, and the following entry was made in his record book, which is still preserved at Stockton:

Die Saturni Apr. 7th, 1827

No. 30

Mr. Hixon

Sulphurata Hyperoxygenata Frict.	100
Tin Case 2d.	1.2

The fact that the sale was a credit transaction, No. 30, indicates that Walker had been making and selling his matches for some time prior to the date of this transaction. The discovery of Walker's record book in 1890 threw considerable light on the background of his invention, showing that his accomplishment in making and selling a match that could be used with a modicum of safety may have been an apparent outgrowth of experiments that he had been conducting for some time on "percussion powder," which consisted principally of potassium chlorate and antimony sulfide. Entries in the record book show that Walker had made several sales of such percussion powder in 1827. The old-fashioned flint lock method of discharging firearms had just been superseded by the percussion cap, and mixtures of chlorate and antimony were suitable for this purpose.

Additional entries show that Walker had sold "oxygent[d] matches" tipped only with chlorate and sugar, which would indicate that such matches were intended for use with a phial of sulfuric acid in an instantaneous light box, as oxymuriated matches. Therefore, the fact that he had made such matches in addition to percussion powder indicates that the idea of a combination of the two principles into one integral friction match may not have been an accident, but a carefully studied and planned procedure. According to an account published in 1857 in a local English newspaper, however, Walker's invention resulted through accidental ignition of some "lighting mixture" that he had prepared for his own use, but which had accidently fallen upon the hearthstone and become ignited.

An analysis conducted on some of Walker's early matches by Professor W. A. Bone confirmed the presence of potassium chlorate, antimony sulfide, gum, and starch (*12*). Walker's matches were made of thin splints of wood, three inches long, tipped with the above mixture of materials. With each metal case of matches was included a piece of "glass paper," folded in two, for use in igniting the matches. A total of 168 recorded sales was listed in Walker's record book between the years 1827 and 1829. In the latter year the fame or notoriety of his matches reached London, it being reported that Faraday exhibited some of them during one of his lectures. A descriptive article relating to Walker's achievement was also published in *The Quarterly Journal of Science, Literature, and Art.*

Because of his retiring nature, Walker either refused or neglected to patent his invention. In 1829 a young chemist named Samuel Jones made and sold imitations of Walker's matches, calling them *Lucifers* (*14*). Jones, who may have received his inspiration from Faraday's lecture, advertised his goods by stating that they had been "lectured upon" at the London and Royal Institutions. Jones was the first match maker to sell his product in small rectangular cardboard boxes, of similar size and shape to those now used for penny matches. The term "lucifer," which was probably original with Jones, remained a popular synonym for matches of various types for a great many years after the original friction match was outmoded and all but forgotten. Walker refused to call his matches by this name, and continued to refer to them as friction lights or "attrition lights" until he stopped making them in 1830.

To ignite one of Walker's friction lights, it was necessary to place the head of the match between folds of sandpaper, nip it tightly between thumb and forefinger, and forcibly withdraw it, trusting in the meantime that the head would not become detached from the splint. The force required to ignite one of the matches by drawing it across sandpaper would have broken the splint. Often the heads were pulled off of several matches before the user succeeded in obtaining a light. Ignition was accomplished generally with explosive violence and the promiscuous showering of sparks and burning particles in all directions. The first matches were not sulfured in order to facilitate transmission of the flame from the burning tip to the splint. Sulfur dipping was soon introduced, however, and it was not long until a majority of the matches were given this essential treatment, camphor being added by a few of the more enterprising manufacturers in order to give the burning product a more pleasant odor.

It is reported that in addition to the objections already noted regarding the showering of sparks and the pulling off of the heads from the splints, the sulfur-antimony vapors "were extremely sensitive to persons with weak lungs" (*4*). Early directions for use, printed on a box of Jones' lucifers, included the following admonition:

> "If possible, avoid inhaling gas that escapes from the combustion of the black composition. Persons whose lungs are delicate should by no means use the lucifers."

Lucifer compositions probably became more effective in 1829, when Isaac Holden showed that a small addition of free sulfur to the other constituents much assisted the ignition (*13*).

EARLY LUCIFER MATCH COMPOSITIONS

Material	*English 1832–1833*	*French 1832–1833*
Sulfur	6.5%	12.5%
Antimony sulfide	24.6%	18.1%
Potassium chlorate	27.6%	41.0%
Ferric oxide	5.6%	3.5%
Gum arabic	35.7%	24.9%

In the United States, probably the first manufacturer to produce matches of the lucifer type in any quantity was Ezekial Byam. The lucifer was short lived, however, it soon being discovered that a match of similar appearance but with much easier striking properties and better controlled ignition characteristics could be made with white or yellow phosphorus as the active ingredient.

(To be continued.)

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Women in "American Men of Science"

A Tabular Study from the Sixth Edition

ALICE WUPPERMAN[1] *The University of Texas, Austin, Texas*

CERTAIN information has been compiled and tabulated concerning the women listed in "American Men of Science"[2] with a view to using it as an indication of whether or not it is advisable for women

[1] Present address: 411 West 116th Street, Box 228, New York City.

[2] CATTELL AND CATTELL, "American men of science," 6th ed., The Science Press, New York City, **1938**.

TABLE 1

NUMBER OF WOMEN ENGAGED IN VARIOUS FIELDS AND TYPES OF WORK

*Field**	*Teacher†*	*Research Worker‡*	*Physician*	*Government Service§*	*Technical Worker‖*	*Miscellaneous¶*	*Retired*	*Not given*	*Total*		*% of 800*	
Chemistry	99	41		9	11	6	3	2	171		21.37	
Biochemistry	17	10	2	4	5			1	39		4.87	
Physical chemistry	6	2			1				9		1.13	
Physiological chemistry	4			2					6		0.75	
Food chemistry	1	1							2	227	0.25	28.37%
Bacteriology	28	88	1	13	9	1			60		7.50	
Biology	18	4		4	1	2			29		3.63	
Cytology	6	1						1	8		1.00	
Histology	4				1				5		0.63	
Botany	83	13		6	3	4	2	2	113		14.13	
Plant pathology	2	2		4					8		1.00	
Plant physiology	3	1		1					5		0.63	
Zoölogy	67	14		2	5	1	1	2	92		11.50	
Physiology	28	5	1	1	4			4	43		5.38	
Entomology	4	2		3		1			10		1.25	
Genetics	5				2				7		0.88	
Embryology	2								2	382	0.25	47.75%
Anatomy	17	2	1						20		2.50	
Pathology	10	3	2				1		16		2.00	
Medicine	1		3			1			5		0.63	
Internal medicine	2		2	1					5		0.63	
Comparative neurology	1								1		0.13	
Dermatology		1							1		0.13	
Pharmacology	1								1		0.13	
Psychiatry			1						1	50	0.13	6.25%
Geology	12	2		2	2				18		2.25	
Archeology						1			1		0.13	
Ethnology		1							1	20	0.13	2.50%
Physics	31	5		4					40		5.00	
Astronomy	9	5			2				16		2.00	
Optics		1							1	57	0.13	7.13%
Nutrition	39	6		3	4				52		6.50	
Home economics	9	1							10	62	1.25	7.75%
Mathematics	1								1		0.13	
Physical metallurgy					1				1	2	0.13	0.25%
Totals	510	131	13	59	51	17	7	12		800		100.00%
% of 800	63.75	16.37	1.63	7.37	6.37	2.13	0.88	1.50				

* The terms used in giving the fields of work are those given in the book.
† Includes "professor," "dean," "head of department," etc.
‡ Includes various types, from "research associate" to "director of research."
§ Includes research workers and technical workers in federal and state bureaus of all sorts.
‖ Includes such designations as "chemist," "technician," "bacteriologist," "analyst," "dietitian," and "metallurgist."
¶ Includes "curator," "librarian," "legal or patent worker," "writer," "editor," "secretary," and perhaps others.

students to undertake the study of chemistry as a major field. It was decided to tabulate only the fields of work, the type of work in each field, and the degrees held.

There were 800 women listed out of a total of 28,000 entries (2.9 per cent). These have been divided into various fields of work. Table 1 shows these, with the number of women engaged in each type of work in the different fields.

As may be seen from Table 1, the greatest number of women listed have done their work in some branch of biology, 382 out of 800, or 47.75 per cent, giving some branch of botany, zoölogy, or biology. The next greatest number are in chemistry, 171 giving "chemistry," and a total of 56 giving some branch of chemistry. This makes a total of 227 out of 800, or 28.37 per cent.

The number of women in each field is given in descending order in Table 2.

TABLE 2

NUMBER OF WOMEN ENGAGED IN EACH FIELD OF WORK

Chemistry	171
Botany	113
Zoölogy	92
Bacteriology	60
Nutrition	52
Physiology	43
Physics	40
Biochemistry	39
Biology	29
Anatomy	20
Geology	18
Astronomy	16
Pathology	16
Entomology	10
Home economics	10
Physical chemistry	9
Cytology	8
Plant pathology	8
Genetics	7
Physiological chemistry	6
Histology	5
Internal medicine	5
Medicine	5
Plant physiology	5
Others	13
	800

The preponderance of chemists was somewhat surprising, as one might suppose that the number of women would be greater in bacteriology, botany, home economics, etc. However, according to a statement in the preface to the book, the approximate order of decreasing frequency in the book as a whole (men and women) is as follows: chemistry, physics, zoölogy, botany, geology, mathematics, pathology, astronomy, psychology, physiology, anatomy, and anthropology.

From Table 1 also may be seen that the type of work offering greatest opportunity of recognition for women is teaching; of the 800 women listed, 510, or 63.75 per cent, were teachers. The only types of work in which teachers did not predominate were medicine, with 3 physicians and one teacher; plant pathology, with 4 in government service and 2 teachers; and psychiatry, archeology, ethnology, optics, and physical metallurgy, with one each, none of whom were teachers. The type offering next greatest opportunity is that of research worker, 131, or 16.37 per cent of the women being listed under that heading. Next comes government service, with 59, or 7.37 per cent of the women being listed under this heading. Government service of course includes many research workers.

From Table 3 may be seen that by far the greater number of women who have attained prominence in scientific fields hold the doctorate degree—611 having the Ph.D., 39 the M.D., and 18 the Sc.D.—a total of 668 out of 800.

Apart from any consideration of the scientists listed in "American Men of Science," the number of women active in such fields as home economics, biochemistry, and bacteriology is probably much greater than those in the physical sciences. But the data here given show that, other things being equal, the probability of attaining prominence is greatest in chemistry, being 17 times as great in chemistry as in home economics, and more than three times as great as in nutrition.

Thus we may conclude that the most favorable types of scientific work available to women are teaching, research work, or government service, in the following fields: chemistry, botany, zoölogy, bacteriology, or nutrition. The possession of an advanced degree, and all that it implies, increases the probability of a woman's attaining prominence in scientific work.

TABLE 3

DEGREES HELD BY WOMEN IN VARIOUS FIELDS

	Ph.D.	*Sc.D.*	*M.D.*	*Masters*	*Bachelors*	*None given*	*Total*
Chemistry	140	3	1	22	4	1	171
Biochemistry	35	1		3			39
Physical chemistry	8			1			9
Physiological chemistry	5				1		6
Food chemistry	2						2
Bacteriology	37	5	9	5	3	1	60
Biology	19		1	9			29
Cytology	6			2			8
Histology	4		1				5
Botany	90	2		15	6		113
Plant pathology	3			4		1	8
Plant physiology	4				1		5
Zoölogy	76	2		9	3	2	92
Physiology	34	2	5	1	1		43
Entomology	7			1	2		10
Genetics	6	1					7
Embryology	2						2
Anatomy	14		4	2			20
Pathology	4		11	1			16
Medicine	2		2		1		5
Internal medicine	1		4				5
Comparative neurology	1						1
Dermatology	1						1
Pharmacology	1						1
Psychiatry			1				1
Geology	16				2		18
Archeology	1						1
Ethnology				1			1
Physics	27			11	1	1	40
Astronomy	10			4	2		16
Optics	1						1
Nutrition	45			6		1	52
Home economics	8	1		1			10
Mathematics	1						1
Physical metallurgy		1					1
Totals	611	18	39	98	27	7	800
% of 800	76.38	2.25	4.88	12.25	3.38	0.86	

Demonstrations Involving Photography

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SINCE every third freshman is probably an enthusiastic amateur photographer, demonstrations involving chemistry in photography should be welcomed. A number of such experiments will be described; with slight modifications they may be performed by the students themselves.

The lecture room need not be light-tight; pulling down the shades and substituting amber for white lights is sufficient.

1. DEMONSTRATIONS EXPLAINING THE CHEMISTRY OF PHOTOGRAPHY

(*A*) *Development* (Illustrating an active reducing agent converting Ag^+ to Ag^0). Bright light. To 100 cc. $N/100$ $AgNO_3$ add 100 cc. $N/100$ NaCl. Before the suspension of AgCl has a chance to separate out, add 10 cc. inorganic developer (*a*) (See formulas at end of article). Reduction to metallic silver should take place almost instantaneously at 20°C. An inorganic developer is chosen here because of simplicity of explanation.

(*B*) *Fixing* (Illustrating the solvent effect of $Na_2S_2O_3$ on AgCl). Bright light. To 100 cc. $N/100$ $AgNO_3$ add 100 cc. $N/100$ NaCl. Then quickly add 60 cc. $N/3$ $Na_2S_2O_3$. At 20°C., clearing should take place in about three seconds. A discussion as to the chemical and physical nature of this solution is advantageous.

(*C*) *Normal Printing Processes.* In advance prepare a synthetic negative as follows: On one half of a piece of glass which will fit a printing frame (4″ × 5″ or larger, depending on size of audience) paste gummed black letters to read "Black on white," while on the other half, with black paint, blacken out all except the letters "White on black." Amber light. Expose a sheet of *Azo F2*[1] paper behind the negative as follows: Distance from 100-watt white light bulb without reflector 6 feet. Time, 5 seconds. The gummed letters should be in contact with the sensitive side of the photographic paper. Develop in metol developer (*b*), or any standard paper developer (D64, D72, etc.) for 3 minutes at 20°C. Rinse in acid short stop bath (roughly $N/5$ acetic acid). Then "fix" in fixing bath (*c*) or any standard fixing bath, for 3 to 5 minutes, after which, if all other unexposed sensitive paper has been covered, the bright light can be turned on. The result will be a paper negative of the glass negative, making a positive, as the legend will show.

This experiment can be modified as follows:

1. The glass negative can be printed when it is reversed (*i. e.*, when the gummed letters are not in contact with the sensitive side of the paper) which will cause the legend to read from right to left.

2. Proper exposure time and/or distance can be determined by varying one at a time and developing for the proper time.

3. Fogging effect caused by leaving the properly exposed print in the developer too long can be shown. This will, of course, illustrate that even the unexposed silver halide is reducible by the developer.

(*D*) *Reversal Printing* (Illustrating the making of a positive directly, a method used in processing amateur cinematographic film and Dufay color films). Repeat *C* exactly as above, up to the immersion in the short stop bath. Remove the developed print from the developer, wash in water, then place in bleaching bath (*d*), leaving it there until all of the black Ag^0 has been oxidized to soluble Ag_2SO_4. Remove, rinse in water, and immerse in a 2–5 per cent $NaHSO_3$ solution to remove any MnO_2 stain formed. Now the bright lights may be turned on. Expose the bleached print, which still has light-sensitive silver halides on it, to bright light (in this case exposure time, distance, etc., are not critical), develop (here developing time is not of great consequence), rinse, fix, and wash. This should lead to a print which is truly "Black on white" and not a negative as was the case in *C*.

(*E*) *Toning* (Illustrating the replacement of metallic Ag by other metals or by colored insoluble salts). Preliminary experiments may consist in demonstrating that (1) Ag^0 plates out Au^0 from a borax solution of $AuCl_3$; (2) $Fe^{+3} + Fe(CN)_6^{-4} \rightarrow$ blue ppt.; (3) $Cu^{+2} + Fe(CN)_6^{-4} \rightarrow$ red ppt.; (4) $2Ag^0 + S^{-2} \rightarrow Ag_2S$, brown-black. Then show the application of these facts by the following photographic processes.

Expose, develop, fix, and wash a sheet of paper exactly as indicated in *C* except that the glass negative is omitted. Cut into many sections and in bright light perform these toning operations:

1. Gold Toning.—Place numbered or labeled sections of the black print into gold-toning bath (*e*) for 1, 2, 3 ... 10 minutes at 20°C. Wash thoroughly and dry; and note how the color of the deposit has changed from black through red-brown to purplish black.

2. Iron (Blue) Toning.—Place numbered sections in iron-toning solution (*f*) for 1, 3, 5, 7, and 9 minutes at 20°C. Remove, rinse, and note how the dried prints range from black to blue. This illustrates that $K_3Fe(CN)_6$ oxidizes Ag^0 to insoluble colorless $Ag_4Fe(CN)_6$, which, by double decomposition, reacts with Fe^{+3} to form insoluble $Fe_4[Fe(CN)_6]_3$.

3. Copper (Red) Toning.—Place numbered sections in copper-toning solution (*g*) for 1, 3, 5, 7, and 9 minutes at 20°C. Wash in distilled water. The tones should range from cold brown to red. As before, the Ag^0 is oxidized, and by reaction with Cu^{+2}, forms insoluble red cupric ferrocyanide.

4. Sulfide (Sepia) Toning.—Place numbered sections in 20 per cent solution of $Na_2S_2O_3$ for 5 minutes at 20°C.,

[1] From here on, all exposure and development times will be mentioned in terms of this paper. Correct exposure for other papers can be determined readily.

then, *without* rinsing, immerse in 3 *N* HCl for 15, 30, 45, and 60 minutes at room temperature. The finely divided S formed on acidification of the $Na_2S_2O_3$ oxidizes the metallic Ag^0 to insoluble Ag_2S, sepia.

(*F*) *Intensifying the Silver Deposit.* Amber light. The film needed is 35-mm. "positive" film, which is slow and non-panchromatic. By means of resistance cut down the intensity of a white electric light bulb until the proper exposure, at say 10 feet, is 32 seconds, when developed in developer (*b*) or any other film developer (DK20, D76, etc.) for 3 minutes at 20°C. The determination of proper time and distance of exposure is best done by the "hunt and pick" method. Having found the proper conditions, cut off seven inches of positive film and expose the entire strip for one second, move an opaque card down one inch and expose the remaining six inches for another second; move the cover down another inch and expose the remaining five inches for two seconds more, move down an inch and expose for four additional seconds, another inch and expose for eight seconds more, another inch for an additional 16 seconds, and finally expose the last inch for an additional 32 seconds. The film then has been exposed in a systematic method from one to 64 seconds as follows: 1, 2, 4, 8, 16, 32, and 64 seconds. Also expose another strip of positive film under the same conditions, but only for 8 seconds. This latter strip will be decidedly underexposed. Develop both strips simultaneously in the same developer for 3 minutes at 20°C. Rinse, fix, and wash. One strip should be uniformly gray, because it is underexposed, while the second should be increasingly darker in graduated steps, where the exposure of any given step is related to that of its neighbors by a factor of 2. Now bright lights can be turned on. Cut the uniform gray negative into four parts.

1. Mercury Intensification.—Thoroughly wet one section of the gray negative and immerse in the mercury bleach (*h*) until clear. (Care! This solution contains $HgCl_2$, very poisonous, and also very irritant to sensitive skins. Perhaps use rubber gloves.) The reaction is:

$$Ag^0 + HgCl_2 \rightarrow AgHgCl_2 \downarrow \text{ (white)}$$

Then wash the film and place in developer (*b*) for 3 minutes at 20°C. Here the organic reducing agent in the developer reduces the silver mercurous chloride to metallic mercury (and perhaps silver too). Rinse, fix, and wash; and compare the dry negative with the original. Even though only one atom of mercury were formed for an atom of silver, the negative would be more dense, for black mercury is more opaque than black silver. Casual visual inspection may not show that the intensified negative is actually more opaque—it may take the third part of this demonstration to show that such is the case.

2. Physical or Silver Intensification.—The bath used here has $AgNO_3$ and a mild organic reducing agent, which thus liberates colloidal Ag^0 slowly. These particles form around the silver deposit on a negative more easily than they do in the solution or on the clear places on the negative. Thus if a negative is immersed in this bath, the deposit of silver on the negative increases, apparently without a change in contrast.

Place two more developed and fixed sections of the thin negative in the *freshly made* physical intensifying bath (*i*) leaving one for 10 minutes and the other for 20 minutes at 20°C. Rinse well, then immerse in a 30 per cent solution of $Na_2S_2O_3$ for two minutes. Wash thoroughly and dry. Too long immersion of a developed film in "hypo" might decrease the amount of silver deposit.

The two physically intensified negatives can be compared with the original control to see whether there has been an increase in the opacity. Perhaps conclusions can be drawn as to the relative merits of the two intensifying processes. Label each of the four sections and save for part 3 below.

3. Proof of Intensification.—The proof should be in the printing. In amber light, place as negatives the step wedge, the control, and the three intensified sections in intimate contact with a sheet of sensitive paper. This can be done between two pieces of clean glass, or in a regular printing frame. Properly expose to white light, develop, and fix. Now by comparison with the step wedge and with each other, conclusions can be drawn as to whether intensification actually took place, and at least roughly quantitatively, as to the merits of the two processes. Remember that going from one step in the wedge to the next darker means doubling the deposit of silver. The step wedge is saved for future experiments.

(*G*) *Reducing the Quantity of Silver Deposit.* It frequently happens that, due to incorrect exposure or incorrect development, or both, the negative is too dense. The contrast of the negative may or may not be correct, but the silver is too thick, thus making for an excessively long printing time. Not only can the amount of silver per square centimeter be lessened, but it can be done proportionally (no change in contrast), superproportionally (decreasing contrast), or subproportionally (increasing contrast).

In amber light, expose four strips of positive film exactly as in *F* above except that if it were found that 32 seconds was the correct exposure time, expose half of each film for 64 seconds and the other half for 16 seconds. After development in a developer for three minutes at 20°C., rinse, fix, and wash. Part of each negative will be overexposed, the other part underexposed, the contrast being 1:4. Now intensification may be performed in bright light.

1. Subproportional Reduction.—Place one of the negatives in subproportional reducer (*j*) for 1–4 minutes at 20°C., or until noticeable reduction has taken place. Wash and dry. The $K_3Fe(CN)_6$ has again formed $Ag_4Fe(CN)_6$ which is soluble in the NH_4CNS, also a constituent of the reducer. Thus some silver dissolves.

2. Superproportional Reduction.—Place the second of the negatives in superproportional reducer (*k*) for 1–4

minutes at 20°C., then wash and dry. The $(NH_4)_2S_2O_8$ oxidizes the Ag^0 to soluble Ag_2SO_4.

3. Proportional Reduction.—Place the third of the negatives in proportional reducer (*l*) for 1–3 minutes, then remove any MnO_2 stain by immersion for a minute or so in a one per cent solution of sodium metabisulfite. Rinse well and dry. This reducer, as the formula shows, is really a mixture of two reducers, one for increasing contrast and the other decreasing contrast.

4. Proof of Reduction and Contrast Change.—In amber light place the three reduced negatives, the control, and the step wedge in the printing frame, in contact with a sheet of photographic paper. Properly expose to white light, develop in paper developer for 3 minutes at 20°C., and compare the results. Not only should the prints of the reduced negatives be darker, but as ascertained by the step wedge, there should be a change in contrast in two cases.

(*H*) *Commercial Silver Recovery from "Exhausted" Fixing Bath.* (Illustrating the electrochemical series and electrodeposition.) Bright light. To some greatly used fixing bath (1) add 1–2 g. Na_2S per liter of bath, forming extremely insoluble Ag_2S, (2) add metallic zinc, (3) electrodeposit the silver on a cathode. Negative film contains about one mg. and positive film about 0.3 mg. of Ag per $cm.^2$, 75 per cent of which finds its way eventually into the fixing bath.

2. CHEMICAL PRINCIPLES EXPLAINED BY PHOTOGRAPHIC EXPERIMENTS

(*A*) *Rates of Reaction.*

1. Effect of Temperature, with Glycine Developer.—Amber light. Expose a sheet of photographic paper for 5 seconds, 5 feet from a 100-watt bulb. Cut into five strips and label on the back with a lead (not indelible) pencil as follows: 10°C., 15°C., 20°C., 25°C., and 35°C. Develop in 300 cc. of glycine developer (*m*) to which one per cent KBr has been added to the extent of one part bromide solution to 15 parts water, for precisely 3 minutes at exactly the temperatures indicated above. The same developing solution can be used merely by heating or cooling, as needed. Rinse the developed paper in short stop (*N*/5 acetic acid). Fix and wash all sections in *exactly* the same way. When dried there should be a noticeable difference in the amount of silver produced.

2. Effect of Temperature, on a Number of Developers.—Repeat 2*A*-1, using metol developer (*b*). Everything else should be exactly the same. When the prints are dried, find one in the glycine series which is just as black as one in the metol series. Call these your standards. Then see whether the metol and glycine prints, developed in each case at 5°C. lower temperature than the standard, are also equally black. If not, the "temperature coefficients" of the two developers are not the same, at least in that temperature range.

3. Effect of Concentration.—In these demonstrations the only variable will be the concentration of the developer. In amber light, properly expose a sheet of photographic paper. Develop labeled sections for 3 minutes at 20°C. in glycine developer (*m*) to which 10 per cent KBr solution has been added to the extent of one part solution to 15 parts developer, and which has been subsequently diluted successively so that the solution employed is $1/2$, $1/4$, $1/8$, $1/16$, and $1/32$ of its original strength. Rinse, fix, and wash as usual. A marked change should be noted in the amount of black silver produced.

If this experiment were repeated with the glycine developer (*m*) without the bromide, interesting results might be obtained. Not only would the most dilute developer produce the least amount of silver, but the color of the silver might be sepia, in place of black. That is probably due to the size of the silver particles produced, colloidal silver having many different colors.

4. Effect of pH. Positive Catalysis.—This is really a demonstration to show the effect of a pH change on development rate. Amber light. Properly expose a sheet of paper. Cut into sections, which are then numbered. Develop the first in 250 cc. of a non-buffered developer (*n*) for 3 minutes at 20°C. Rinse, fix, and wash. Develop the second section in the same developer, to which has been added 2 cc. concentrated HCl, maintaining all other factors constant. Rinse, fix, and wash. Repeat using 2 cc. more of the concentrated HCl, and finally 4 cc. more HCl. Even when 10 cc. of concentrated HCl have been added the pH is still greater than 7. For those interested in photography, this demonstration shows the need for controlling the alkalinity of the developer, and explains why immersion of the print, wet with developer, into the acid short stop, stops development. For all of the students, it shows that this particular reducing agent works faster, the more alkaline the solution.

5. Effect of KBr. Inhibition.—Those who develop their own films know that the presence of KBr in the developer appreciably slows down development rate. That fact will be used here to illustrate negative catalysis, although that is probably only part of the answer.

Amber light. Expose a sheet of paper properly. Cut into sections and label. Develop one strip for 3 minutes in 250 cc. half-strength developer (*m*) to which has been added $1/4$ cc. of 10 per cent KBr. Rinse, fix, and wash. Develop the other strips exactly the same way, except that KBr solution has been added in $1/4$-cc. steps until the final developer has in it 1.5 cc. KBr solution.

(*B*) *Quantity of Silver Produced.*

1. Effect of Exposure Time.—In amber light, properly expose a small piece of the same paper, at the same distance from the same bulb, but at $1/10$, $2/10$, $3/10$ . . . $9/10$ the proper exposure. Develop all of them in the same paper developer for exactly the same length of time and at the same temperature. Rinse, fix, and wash. The photographers in the class will recognize what they already know, *i. e.*, that the amount of Ag^0 produced depends on exposure time, all other factors being kept constant. Those not particularly interested in photography will see that the intensity of the latent image

produced is a function of the energy received from the light source.

2. Effect of Color of Light. Photosensitizers.—In absolute darkness, expose a sheet of paper to the light filtered by a deep amber filter (cellophane or glass) for a few seconds. In complete darkness develop properly in a paper developer, rinse, fix, and wash, turning on the amber light as soon as the paper has been in the fixing bath for three minutes.

Repeat exactly, but before exposing the paper to the filtered light, sensitize it. This is done by swabbing the paper for several minutes in absolute darkness with sensitizing solution (*o*), after which wash well with distilled water, then immerse in 95 per cent alcohol and dry rapidly (all operations in absolute darkness, of course).

Those students who are familiar with photographic principles realize that this experiment demonstrates the making of panchromatic and orthochromatic films from emulsions blind to certain radiations. The theory of sensitizers and desensitizers is given in Clerc, Neblette, and Henney-Dudley, as well as in other standard texts on photography.

3. Effect of Ammonia.—Expose a sheet of paper for one-tenth the proper exposure. Cut into three sections. Paint three desiccators with black asphaltum until they are light-tight. Place in one desiccator concentrated H_2SO_4, in the second a few cc. of concentrated NH_4OH, and in the third water. Allow a piece of the exposed paper to remain in each desiccator for a short time. Then develop the three sections in exactly the same way, in the same developer for the same length of time. Rinse, fix, and wash by the same procedure. There should be a change in the quantity of silver produced. The use of NH_3 in increasing the speed of an emulsion is used commercially with films, although the NH_3 is usually applied before, rather than after the exposure.

FORMULAS

(*a*) Inorganic Developer

Sodium bisulfite	30.0 g.
Sodium hydrosulfite	20.0 g.
H_2O to make	1.0 liter

(*b*) Metol Developer

H_2O (52 °C.)	500.0 cc.
Metol	6.2 g.
Sodium sulfite, anhydrous	45.0 g.
Sodium carbonate, anhydrous	67.5 g.
Potassium bromide	1.9 g.
H_2O to make	3.0 liters

(*c*) Fixing Bath

Water	2.0 liters
Sodium thiosulfate	480.0 g.

When thoroughly dissolved, add the following solution slowly to the cool thiosulfate solution while stirring the latter rapidly:

Water at 52 °C	160.0 g.
Sodium sulfite, desiccated	30.0 g.
Acetic acid (28% pure)	96.0 cc.
Potassium alum	30.0 g.

(*d*) Bleaching Bath

An aqueous solution which contains 0.4% of both $KMnO_4$ and H_2SO_4.

(*e*) Gold-Toning Bath

Sodium acetate, fused	10.0 g.
Borax	1.0 g.
Gold chloride (1% solution)	25.0 cc.
H_2O to make	1.0 liter

(*f*) Iron-Toning Bath

Ferric ammonium citrate (10% solution)	60.0 cc.
$K_3Fe(CN)_6$ (10% solution)	60.0 cc.
Acetic acid (10% solution)	600.0 cc.

(*g*) Copper-Toning Bath. Mix equal volumes of No. 1 and No. 2.

No. 1		No. 2	
$K_3Fe(CN)_6$	3.2 g.	$CuSO_4$	4.0 g.
Potassium citrate	16.0 g.	Potassium citrate	16.0 g.
H_2O to make	600 cc.	H_2O to make	600.0 cc.

(*h*) Mercury Bleach

Potassium bromide	22.5 g.
Mercuric chloride	22.5 g.
H_2O to make	1.0 liter

(*i*) Physical Intensifying Bath

Crabtree and Muehler[2] recommend:

Solution 1

Silver nitrate	60.0 g.
H_2O to make	1.0 liter

Solution 2

Sodium sulfite (desiccated)	60.0 g.
H_2O to make	1.0 liter

Solution 3

Sodium thiosulfate crystals	105.0 g.
H_2O to make	1.0 liter

Solution 4

Sodium sulfite (desiccated)	15.0 g.
Metol	24.0 g.
H_2O to make	3.0 liters

To prepare the intensifier, add one part of solution (1) slowly to one part of solution (2), obtaining a thorough mixture by stirring or shaking. A white precipitate will form which is dissolved by the addition of one part of solution (3). The resulting solution should be permitted to stand until clear, after which three parts of solution (4) should be added, with constant stirring. The film should be treated immediately in this solution. This mixed solution is stable for about 30 to 45 minutes at 20 °C.

(*j*) Subproportional Reducer

Potassium ferricyanide	5.0 g.
Ammonium sulfocyanate	10.0 g.
H_2O to make	1.0 liter

(*k*) Superproportional Reducer

H_2O	500.0 cc.
Ammonium persulfate	60.0 g.
Concentrated H_2SO_4	3.0 cc.
H_2O to make	1.0 liter

(*l*) Proportional Reducer

NIETZ AND HUSE REDUCER

Solution 1

Potassium permanganate	0.25g.
Sulfuric acid (10 %)	15.0 cc.
Distilled water to make	1.0 liter

[2] CRABTREE AND MUEHLER, "Reducing and intensifying solutions for motion picture film," *J. Soc. Motion Picture Engrs.*, **17** (No. 6), 1001–53 (1931).

Solution 2

Ammonium persulfate	25.0 g.
Distilled water to make	1.0 liter

For use, one part of solution (1) is added to three parts of solution (2). The keeping properties of the combined solutions are very poor so the solutions should be mixed immediately before use.

(*m*) Glycine Developer

Sodium sulfite, anhydrous	15.0 g.
Potassium carbonate	45.0 g.
Glycine	10.0 g.
H_2O to make	1.0 liter

At time of use dilute to 1/6 strength

(*n*) Non-buffered Developer

Sodium sulfite, anhydrous	187.0 g.
Metol	21.5 g.
Hydroquinone	43.0 g.
Sodium hydroxide	43.0 g.
H_2O to make	1.0 liter

(*o*) Sensitizing Solution

Ethyl alcohol (95%)	40.0 cc.
Pinacyanol stock solution (0.1%)	4.0 cc.
Concentrated NH_4OH	2.0 cc.
H_2O	60.0 cc.

Editor's Note: Readers may be interested in referring to previous articles on photography which have appeared in the JOURNAL OF CHEMICAL EDUCATION:

ALYEA, "Lantern slide technics," **16,** 308 (1939).
CARROLL, "The preparation of photographic emulsions," **8,** 2341 (1931).
DUNBAR, "The photographic club," **14,** 91 (1937).
FLIEDNER, "A chemistry club project in photography," **11,** 620 (1934).
GOLDBLATT AND BATES, "Preparation of lantern slides without a camera," **17,** 462 (1940).
GURINSKY, "A camera for photographic demonstration," **17,** 432 (1940).
MACLEAN, "A project for general chemistry students: color toning of photographic prints," **14,** 31 (1937).
MURRAY AND HANSON, "Coloring snapshots with organic dyes," **17,** 430 (1940).
SCHUMACHER, "Photography in the college curriculum," **17,** 427 (1940).
SHEPPARD, "The chemistry of photography. I. Historical considerations. II. The latent image. III. Development of negative and positive images," **4,** 298, 465, 749 (1927).
"The chemistry of photographic materials," **6,** 2002 (1929).

The Theory of Solubility Product

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IN THE theory of solubility product there are certain difficulties which are not always mentioned in the textbooks. In the present note these difficulties are examined and it is found that the theory is not very suitable for inclusion in elementary teaching; this is especially the case when the theory is applied to strong electrolytes. It is shown, however, that the phenomena of precipitation, where the theory is most frequently used, can be explained in a simple and satisfactory manner without recourse to the generally erroneous law of the constancy of solubility product.

THE SOLUBILITY PRODUCT THEORY

In the traditional theory, it is supposed that in any solution of an electrolyte there is an equilibrium between dissolved but undissociated electrolyte and the free ions:

$$MA \rightleftharpoons M^+ + A^-$$

and hence by the Mass Action Law, in its simple form,

$$[M^+][A^-] = K[MA]$$

where $[M^+]$ and $[A^-]$ are the concentrations of the ions and $[MA]$ is the concentration of the undissociated molecules. In a saturated solution at fixed temperature and pressure, the quantity $[MA]_s$ is assumed to be a constant, the subscript "s" denoting the condition of saturation. This quantity is called the *molecular solubility* and its constancy is assumed to hold *independently of the presence of any other electrolyte* (referred to below as the *added* electrolyte). It follows that the product $[M^+]_s[A^-]_s$ is also a constant and is called the *solubility product:*

$$[M^+]_s[A^-]_s = S \qquad (1)$$

There are thus three assumptions in the derivation: (1) that the equilibrium between ions and undissociated molecules in solution actually occurs; (2) that the simple Mass Action Law in terms of concentrations can be applied to this equilibrium; and (3) that the concentration $[MA]_s$ of the undissociated part of the solute in a saturated solution is unchanged by the addition of other electrolytes.

The derivation of this law, on the basis of these assumptions, continues to hold in the special case where the saturating electrolyte and the added electrolyte possess common ions. For example, if the substance MB is added and ionizes to give the common M^+ ion, the law gives the reduction in the equilibrium concentration of the A^- ion and hence the reduction in the solubility of MA. This gives a method of testing the law and also its main field of use.

THEORY AND EXPERIMENTAL RESULTS IN THE CASE OF STRONG ELECTROLYTES

The derivation given above is clearly unsatisfactory in the case of strong electrolytes which are now generally believed to be completely ionized. The equilibrium is simply

$$(M^+A^-)_{solid} \rightleftharpoons M^+ + A^-$$

and the theory of solubility product can no longer be

obtained in the manner given above, since this depends on there being a *homogeneous* equilibrium

$$MA \rightleftharpoons M^+ + A^-$$

in the solution, to which the Mass Law can be applied. The simple theory is, therefore, incompatible with the idea of complete ionization and an alternative approach must be looked for. Even if ionization were assumed complete but with only a partial *dissociation* of the ions, a derivation of equation (1) by the above method would still be unsatisfactory. Such an assumption would involve the existence of ion pairs M^+A^- in solution. In place of assuming the constancy of the concentration $[MA]_s$ of the non-existent unionized molecules it would be necessary, according to this idea, to assume constancy in the concentration of the ion pairs. This concentration would be expected, however, to vary considerably with the electrical condition of the solvent and hence with the presence of other electrolytes.

In the case of strong electrolytes, the only sound approach to solubility product is a thermodynamic one. Thus, any two saturated solutions of the electrolyte are both in equilibrium with the solid electrolyte and so, by definition, the thermodynamic mean activity $a_{M^+A^-}$ of the dissolved substance must be the same in both solutions. The mean activity of an electrolyte in a saturated solution is, therefore, a constant at fixed temperature and pressure, independent of the presence of other substances, whether with or without the common ion.

$$a_{M^+A^-} = \text{constant} \tag{2}$$

The mean activity of the strong electrolyte is taken as equal to the square root of the product of the individual ion activities, a_{M^+} and a_{A^-}, so that the following relation holds in any saturated solution of MA:

$$\sqrt{a_{M^+}a_{A^-}} = a_{M^+A^-} = \text{constant} \tag{3}$$

Now, the ion activities are functions of the ion concentrations according to the equations:

$$\begin{aligned} a_{M^+} &= f_{M^+}[M^+] \\ a_{A^-} &= f_{A^-}[A^-] \end{aligned} \tag{4}$$

which are used to define the ion activity coefficients, f_{M^+} and f_{A^-}.

Combining (3) and (4):

$$f_{M^+}f_{A^-}\,[M^+][A^-] = a_{M^+}a_{A^-} = a^2_{M^+A^-} = \text{constant} \tag{5}$$

The activity coefficients of the individual ions are related to the mean activity coefficient of the electrolyte itself by the following relation, similar to the one above relating ion activities to the mean activity:

$$\sqrt{f_{M^+}f_{A^-}} = f_{M^+A^-} \tag{6}$$

From equations (5) and (6) it follows that

$$[M^+][A^-] = \frac{\text{constant}}{f^2_{M^+A^-}}$$

or preferably we should insert the subscript "s," already adopted to denote that the equation applies only to a saturated solution, and write

$$[M^+]_s[A^-]_s = \frac{\text{constant}}{f^2_{M^+A^-}} \tag{7}$$

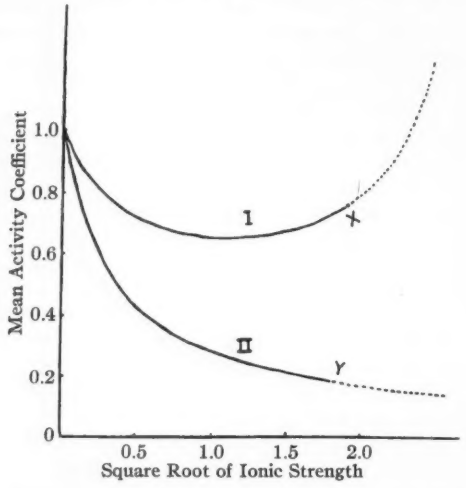
So far the treatment is formal and the question whether the solubility product, $[M^+]_s[A^-]_s$, is itself a constant is seen to depend on the constancy of $f_{M^+A^-}$ in the presence of other electrolytes. Now the mean activity coefficient can be determined by independent experimental methods and is found always to depend on the *ionic strength* of the solution. The ionic strength is defined as follows: The molal concentration of each ion in the solution is multiplied by the square of its valency and these terms are summed together and divided by two. The reason for this procedure is outside the scope of this paper and, for the present purpose, it is sufficient to say that the activity coefficient of any electrolyte is found to depend on a certain function (*i. e.*, the ionic strength) of the concentration and charge of all the other ions in the solution, whether they are common to the original electrolyte or not. It follows, from equation (7), that *the solubility product is not, in general, a constant but depends on the electrical condition of the solvent as modified by other substances.*

It should be mentioned that the ionic strength is not the only factor on which the activity coefficient of an electrolyte depends. Except in very dilute solutions, specific effects are present and the activity coefficient of an electrolyte may have different values at the same ionic strength according to the specific properties of the other ions present in the solution, apart from their charge and concentration.

In very dilute solutions, weaker than 0.001 molar, where the ionic strength is low, the activity coefficient of many electrolytes approaches within a few per cent of unity and varies little with further dilution. The solubility product relation [equation (1)] might be expected, therefore, to be fairly satisfactory for very slightly soluble strong electrolytes when the concentration of all electrolytes present is very low. In more concentrated solutions, where the ionic strength is greater, the activity coefficient is no longer nearly unity but considerably less. This is the case even when the concentration of the electrolyte under consideration is still quite low, but when there is a considerable concentration of some added electrolyte, which has the effect of increasing the ionic strength of the solution. For example, the activity coefficient of a saturated thallous chloride solution at 25°C. is 0.89, but in the presence of 0.1 molar potassium nitrate the saturated thallous chloride has a coefficient of only 0.73. By equation (7) the solubility product is therefore about 50 per cent greater in the latter solution.[1]

[1] All data on thallous chloride are from LEWIS AND RANDALL, "Thermodynamics and the free energy of chemical substances," 1st ed., McGraw-Hill Book Co., Inc., New York City, 1923.

With regard to the present discussion, the activity coefficient curves of electrolytes fall into two main types. These are illustrated in the diagram, which shows the activity coefficient plotted against the square root of the ionic strength. In curves of Type I the



activity coefficient falls to a minimum and then rises with further increase in the ionic strength. On the other hand, in curves of Type II the activity coefficient continues to fall throughout its whole course. The significant difference, with regard to the present discussion, is that in Type I the saturation point of the electrolyte lies on a rising portion of the curve, while in Type II it lies on a falling portion of the curve. Although, as mentioned above, the *numerical* value of the activity coefficient, in solutions of appreciable strength, depends to some extent on the specific character of the other ions present, it does not appear, in general, that the *type* of the curve of an electrolyte, MA, varies with the addition of a second electrolyte, provided the concentration of the latter is not very great.

In the following table a few electrolytes are classified according to whether they give curves of Type I or Type II.

Type I	*Type II*
NaCl	
NaBr	TlCl
NaI	Na_2SO_4
KCl	
KBr	
KI	

Consider the effect of adding a second electrolyte to a saturated solution of a salt, such as thallous chloride, of Type II. The saturated solution of the pure salt has an ionic strength and activity coefficient corresponding to some point such as *Y* on the diagram. The addition of a small amount of a second electrolyte will cause an increase in the ionic strength of the solution and the activity coefficient of the thallous chloride will thus correspond to some point on the dotted continuation of the curve. The activity coefficient will therefore be *lower* than in the pure saturated solution, always providing that the small quantity of the second electrolyte has no considerable specific effect on the shape of the curve.

The reduced value of the activity coefficient will result, according to equation (7), in an *increased* value of the solubility product and the solubility itself is therefore greater in the presence of the added electrolyte. For example, the addition of 0.1 mol of potassium nitrate increases the solubility of thallous chloride by 22 per cent and an equal amount of potassium sulfate increases it by 33 per cent.

The effect of adding a second electrolyte to a strong electrolyte of Type II is thus, in general, to increase the solubility. However, if the second electrolyte possesses a common ion, say Tl^+ in the example considered, this is no longer the case. Here the same increase in the solubility product, $[Tl^+]_s[Cl^-]_s$, is again required, but this is usually more than accounted for by the increased concentration of Tl^+. The concentration $[Cl^-]_s$ must therefore fall and the solubility of the thallous chloride must be less than in a solution of the pure electrolyte. This is the *common ion effect.* For example, the solubility of thallous chloride is reduced 74 per cent by the addition of 0.1 mol per liter of thallous nitrate.

Consider now the case of an electrolyte of Type I where the activity coefficient curve of the pure solution terminates, at the saturation point *X*, on a rising part of the curve. Here the addition of any second electrolyte will increase the ionic strength and will result in an increased value of the activity coefficient along the prolongation of the curve, again provided the added electrolyte has no pronounced specific effect. This results in a decrease in the solubility, according to equation (7), and this decrease occurs whether or not a common ion is added. Unlike the case of electrolytes of Type II, the effect due to the change in ionic strength here works in the same direction as the common ion effect. For example, Harkins and Paine[2] have shown that the solubility of strontium chloride in water is decreased almost to the same extent by the addition of hydrobromic and hydriodic acids, without the common ion, as by the addition of hydrochloric acid. Strontium nitrate, on the other hand, had an almost negligible effect on the solubility of strontium chloride, in spite of the presence of the common ion. This last result is exceptional and can only be due to strontium nitrate having a very pronounced specific effect in modifying the activity coefficient curve of strontium chloride. As mentioned before, the coefficient does not depend solely on the ionic strength.

As a further example there is the precipitation of a saturated sodium chloride solution by the passage of gaseous hydrogen chloride. This is often quoted in the textbooks as an example of the common ion effect and is used in leading up to solubility product. Yet I have found that this gas will also precipitate saturated

[2] *J. Am. Chem. Soc.*, **38**, 2709 (1916).

solutions of sodium and potassium bromides, potassium iodide, and sodium nitrate, none of which possesses with it a common ion. The precipitate, at least in the early stages of the process, was found by analysis to consist mainly of the salts from which the solutions had been made up, *i. e.*, bromide, iodide, or nitrate. A little chloride was also present, being produced by metathesis from the hydrogen chloride.

In another experiment it was found that hydrogen bromide gas will precipitate a saturated solution of a chloride, such as sodium chloride.

It is interesting to examine these precipitations in relation to the activity coefficient curves. The curves for the sodium and potassium halides are all of Type I, for which the addition of any electrolyte to the saturated solutions would be expected to cause precipitation, as actually occurred when hydrogen chloride and hydrogen bromide were the added electrolytes. The activity coefficient curve of sodium nitrate has not been followed right up to the saturation point (about 11 molar at 25°; at 6.0 molar it is still falling) but the fact that it is precipitated by hydrogen chloride suggests that it is also of Type I.

On the other hand, the curve for sodium sulfate resembles that of thallous chloride in possessing no minimum before the saturation point is reached. Precipitation, therefore, would not be expected, except possibly by the addition of a common ion. In agreement with this, hydrogen chloride was passed into a saturated solution of this salt and no precipitate had appeared after ten minutes passage of the gas.

In general, however, it is not possible to make a certain prediction whether, in some particular case, precipitation will occur or not, unless it is known that the added electrolyte has no considerable specific effect on the activity coefficient curve of the saturating salt.

In conclusion, it is seen that quite large variations in the solubility and solubility product of a salt may occur, whether or not the added electrolyte possesses with it a common ion. Moreover, the activity coefficient is seen to be the necessary "correcting factor" to the old form of the solubility product law and the same is shown below to be the case also when weak electrolytes are considered. The activity coefficient is, of course, used for the same purpose with other laws of solution which depend on concentrations for their formulation, such, for example, as Raoult's Law. The ideal law of solubility product constancy is, therefore, of a type with the other limiting laws of solution which are not precisely obeyed, except under very dilute conditions.

The physical cause of the deviations from the ideal has been ascribed, in the Debye-Hückel theory, to the electrical attractions and repulsions between the ions. The magnitude of this effect is not only dependent on the concentration and charge of the ions (*i. e.*, the ionic strength) but also, to some extent, on the degree to which the dielectric constant of the solvent is modified by the presence of the solute and on the nearness of approach of the ions, *i. e.*, on their effective diameters and degree of solvation. Specific effects of the type already discussed can thus arise, especially in solutions of appreciable concentration.

THEORY AND EXPERIMENTAL RESULTS IN THE CASE OF WEAK ELECTROLYTES

The assumption of an equilibrium between ions and unionized molecules in solution is certainly justified in the case of weak electrolytes. However, in the traditional derivation of the solubility product relation, it remains to be considered whether the Mass Law in terms of concentrations may be applied to this equilibrium and whether the concentration $[MA]_s$ of the unionized part of the weak electrolyte remains unchanged by the addition of a second substance.

Now for the equilibrium

$$MA \rightleftharpoons M^+ + A^-$$

the true or thermodynamic equilibrium constant, K_t, can be expressed either in terms of the activities of the species:

$$K_t = \frac{a_{M^+} a_{A^-}}{a_{MA}}$$

or in terms of concentrations and activity coefficients:

$$K_t = \frac{[M^+][A^-]}{[MA]} \times \frac{f_{M^+} f_{A^-}}{f_{MA}}$$

The simple Mass Action Law, in which concentrations only are used, is evidently justifiable only under conditions where the activity coefficient factor, $\frac{f_{M^+} f_{A^-}}{f_{MA}}$, is unaffected by the presence of other substances. As in the case of strong electrolytes, this occurs only when the ionic strength is low. For example, aqueous solutions of aliphatic acids have a value of almost unity for the activity coefficient factor, but in a 0.5 N sodium chloride solution the value of the factor for the aliphatic acid is reduced to only 0.55, with corresponding increase in the quantity $\frac{[H^+][A^-]}{[HA]}$.

The last equation above can also be written as

$$[M^+]_s[A^-]_s = K_t \times \left(\frac{f_{MA}}{f_{M^+} f_{A^-}}\right)_s \times [MA]_s \qquad (8)$$

when it is applied to the saturated solution. For the solubility product, $[M^+]_s[A^-]_s$, to be a constant, it is evident that not only the activity coefficient factor but also the molecular solubility, $[MA]_s$, must be assumed to remain unchanged by the addition of other substances. (It is conceivable that the two factors should vary equally and oppositely. But this is unlikely and does not fit in with experimental data.)

The assumption of constancy in the molecular solubility has not been discussed previously because with strong electrolytes the species MA is not, in any case, present in solution. Where weak electrolytes are concerned, the unionized molecules are certainly present but, in general, the evidence goes to show that their concentration in a saturated solution is very considerably modified by the presence of other substances. This is illustrated by the following data from International

Critical Tables, which give the percentage greater or smaller solubility of hydrogen sulfide and ammonia in aqueous solutions of various substances at 25°C., by comparison with their solubility in pure water at the same temperature.

Hydrogen sulfide	*Ammonia*
−0.5% in *N* HCl	−22% in *N* NaOH
+ 11% in *N* HI	−29% in *N* KOH
− 17% in *N* NaCl	−12% in *N* NaCl

Both hydrogen sulfide and ammonia are extremely weak electrolytes so that the total solubility differs only negligibly from the molecular solubility. The figures show, therefore, the very considerable change in the molecular solubility caused by the presence of a second electrolyte.

The same conclusion holds for non-electrolytes. For example, the solubility of oxygen is 10 to 40 per cent less in normal solutions of various electrolytes than in pure water. This reduction in the solubility of a covalent molecule by the addition of an electrolyte is the very general phenomenon known as *salting out*. It probably arises from causes such as the reduction in the amount of free water by the solvation of the added ions.

Referring now to equation (8), it is seen that both the activity coefficient factor, $\left(\frac{f_{MA}}{f_{M^+} f_{A^-}}\right)_s$, and the molecular solubility, $[MA]_s$, are modified by the presence of a second electrolyte and thus give rise to a lack of constancy in the solubility product. This conclusion is in general agreement with experiment. Kendall,[3] for example, carried out some extensive measurements on the solubility of various weak acids in the presence of added strong acids. His results show that when the concentration of added strong acid is small, the depression in solubility of the weak acid is often in fair quantitative agreement with the solubility product law. As the concentration was increased, however, the solubility of the weak acid was frequently found to pass through a minimum and then actually to increase.

CONCLUSION

The conclusions which have been reached can be summarized as follows. In the first place, the solubility product relation [equation (1)] is to be regarded as a limiting law, only obeyed in practice in the most dilute solutions. Second, the old derivation of the law can no longer be carried out for strong electrolytes which are now believed to be completely ionized. Instead, a thermodynamic expression [equation (7)] can be obtained which reduces to the simple form for very dilute solutions. Finally, in the case of weak electrolytes, the old derivation is less objectionable but it involves considerable approximation in two of its assumptions and a thermodynamic relation [equation (8)] is again to be preferred. This relation also reduces to the simple form under limiting conditions.

[3] *Proc. Roy. Soc. A*, **85**, 200 (1911); *J. Am. Chem. Soc.*, **43**, 1545 (1921).

The question arises of how solubility product should be dealt with in chemical teaching. For elementary classes the thermodynamic approach is, of course, out of the question, but it is suggested that the old treatment is quite adequate for weak electrolytes, as an approximation. For strong electrolytes, however, it is wrong in principle and, in the opinion of the author, should be avoided, together with all the older ideas of incomplete ionization in solutions of these substances.

Now, the theory of solubility product has always found its greatest use in giving an explanation to certain precipitation phenomena and the question arises whether these phenomena can be adequately explained without recourse to the theory. Fortunately this is the case; solubility product theory is expressed in the incorrect *quantitative* statement

$$[M^+]_s[A^-]_s = \text{constant}$$

whereas all that is required is a *qualitative* application of the idea of a reversible reaction. In the precipitation of a sulfide, for example, the equilibrium in solution is:

$$M^{++} + H_2S \rightleftharpoons M^{++} + 2H^+ + S^{--}$$

(the HS^- ion is also present). Now the sulfide is precipitated only if its concentration in solution is raised to the saturation value. Expressed in another way, the M^{++} ions and the S^{--} ions, on the right-hand side of the equation, are deposited together to form the crystal lattice of the sulfide only when their concentrations are sufficiently high. The question of whether or not precipitation occurs depends, therefore, both on the solubility of the particular sulfide and on the concentration of sulfide ions and metal ions in solution. Low solubility and high concentration of ions naturally facilitate precipitation. Now, the concentration of sulfide ions can be reduced by increasing the acidity of the solution. This is simply on account of the mass effect of the hydrogen ion on the reverse reaction as written above, *i. e.*, on the ionization of hydrogen sulfide. It does not matter whether this ionization accurately obeys the Mass Action or Solubility Product Laws.

It follows that, even though the natural solubility of a particular sulfide may be very low, the acidity of the solution may be such as to give too low a sulfide ion concentration to cause precipitation. With respect to the possibility of precipitation, the sulfides then fall into three groups:

(*a*) Sulfides such as those of the Group II analytical separation. These are all extremely insoluble, with the result that conditions leading to precipitation can occur, even though the sulfide ion concentration may be very low on account of the presence of acid.

(*b*) Sulfides of rather higher solubility, such as those of the Group IV separation, whose precipitation can occur only at higher sulfide ion concentrations.

(*c*) Very soluble sulfides, such as sodium sulfide, which are never precipitated when they are formed in solution, even in complete absence of acid, *i. e.*, when the sulfide ion concentration is quite high.

The Quantitative Separation of Some Dyestuffs[1]

An Application of the Chromatographic Method

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THE purpose of this paper is to present a method of chromatographic analysis suitable for performance by college juniors. The method is designed to be fairly rapid and inexpensive, rather than to achieve the greatest accuracy possible.

Water was chosen as the solvent to decrease the expense and the fire hazard. The solutes to be separated and determined are three commercial dyestuffs, *viz.*, victoria blue B, crystal violet, and auramine. Ruggli and Jensen[2] separated these and other dyes qualitatively with specially activated alumina as the adsorbent. In our method, satisfactory results are obtained with Merck's Reagent ignited aluminum oxide just as it comes from the bottle, without any time-consuming activation process.

The apparatus is illustrated in Figure 1. The tube *T*, 15 cm. long, is cut from a combustion tube with an internal diameter of 1.5 cm. Above it is fitted a 50-ml. dropping funnel *F*. The lower end of the tube is connected through a stopcock *S* to a 60-ml. side-arm pyrex test tube *R*, preferably graduated. Suction is applied to *R* through the safety trap *P*. An open-tube mercury manometer (not shown) is connected to *P*.

The tube *T* should be dry at the beginning of a determination. The dropping funnel is removed, and a wad of absorbent cotton (*C* in Figure 1) is put in the bottom of the tube. The cotton is firmly tamped down with a half-inch wooden dowel. The cotton should extend one cm. up the tube. One g. ± 0.1 g. of Johns-Manville's Hyflo-Supercel and 14 ± 1 g. of Merck's Reagent ignited aluminum oxide are mixed by shaking together for two minutes in a dry cork-stoppered wide-mouth bottle. This mixture (*A* in Figure 1) is then transferred to the tube with the aid of a wide-stem funnel. The tube is tapped continually with the dowel during this addition. Then a disc of filter paper, 1.5 cm. in diameter, is placed on top of the adsorbent.

The stopcock *S* is closed, and a vacuum of 20 ± 2 cm. of mercury is applied. Then the stopcock is opened, and the tube is tapped with the dowel a few more times. The height of the column, including the cotton, is 10.6 to 12.3 cm.

The upper part of the tube is now filled with a solution 0.002 *M* with respect to both primary and secondary sodium phosphates. This solution, hereafter called the buffer, has a pH of 7.04. The liquid runs down the tube slowly, displacing most of the interstitial air. More buffer is added to the tube as necessary to keep the column always covered with liquid. As soon as the buffer starts to drop into the receiver, the column of adsorbent is ready for use.

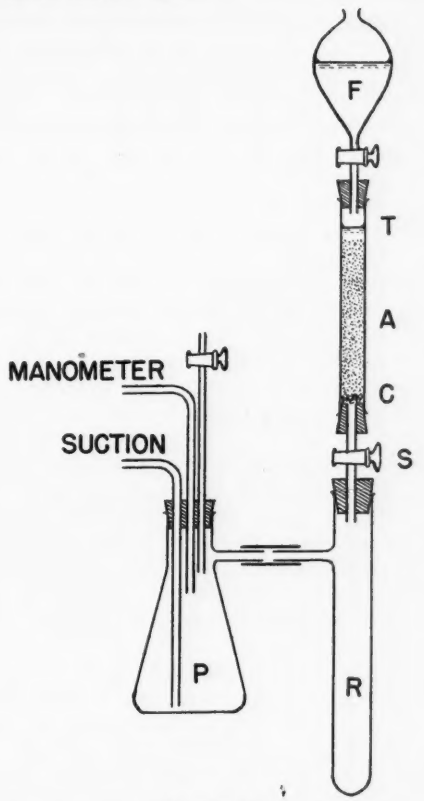

FIGURE 1

Then the stopcock is closed without disturbing the vacuum in the trap. The level of buffer is adjusted to be 2 cm. above the top of the column. Then 0.100 ml. of a solution of the unknown dye mixture in 95 per cent ethanol is added to the tube. The unknowns should be prepared to contain in 0.100 ml. a maximum of 1.00 mg. of total dye and a minimum of 15 γ of each constituent.

After addition of the dye, the stopcock is opened. When the meniscus is about 5 mm. above the top of the column, the upper part of the tube is rinsed down with some buffer from a wash bottle. When the meniscus settles again to about 5 mm. from the adsorbent, the dropping funnel filled with buffer is put in place, and its stopcock is opened. Care must be taken not to let

[1] Presented before the Division of Chemical Education at the 100th meeting of the A. C. S., Detroit, Michigan, September 12, 1940.

[2] RUGGLI AND JENSEN, "Die chromatographische Adsorptionsanalyse in Anwendung auf wässerige Lösungen künstlicher organischer Farbstoffe," *Helv. Chim. Acta*, **18**, 624–43 (1935).

the top of the column be exposed to air. If the vacuum is maintained at 20 cm., the liquid will flow at the rate of 0.7 to 1.1 ml. per minute.

As the dyes descend through the column, the separation occurs. Victoria blue is most tenaciously adsorbed and remains in the upper part of the column. Auramine is least adsorbed and separates as a wide yellow band in the bottom of the adsorbent. Crystal violet, with intermediate adsorbability, forms a distinct band in the center. When the auramine reaches the cotton, the separation is complete. At this point, about 20 to 30 ml. of turbid but colorless filtrate will have been collected. The lower edge of the blue band is 2 to 6 mm. from the top of the column, depending on the composition of the mixture. A white band of thickness varying from a fraction of a millimeter to 10 mm. appears between the blue and purple bands. The lower edge of the purple band is 20 to 74 mm. from the top. No white band separates the purple from the yellow. However, the lower part of the purple zone and the upper part of the yellow zone are relatively poor in the respective dyes. Thus a good separation can be obtained mechanically.

As soon as the auramine reaches the cotton, the stopcock of the dropping funnel is closed, and the funnel is removed. The liquid remaining above the column is allowed to flow into it, and air is then sucked through the column for five minutes to remove the excess liquid. Then the suction is shut off, and the tube is removed.

If drops of liquid remain above the column, they are removed by wiping with a cotton wad on a wooden splint. The small quantity of victoria blue lost in this process is neglected. With the aid of a microspatula, the filter paper and the upper (blue) layer of adsorbent are removed and transferred to a 100-ml. beaker. Care must be taken not to contaminate the blue adsorbent with the violet layer.

Then the upper part of the tube is wiped again with the cotton wad, lest some remaining victoria blue contaminate the crystal violet. The violet layer is then removed and transferred to another 100-ml. beaker. It is impossible to remove all the violet adsorbent without some slight contamination with the auramine. This contamination, however, is not sufficient to interfere with the colorimetric determination of either dye.

The upper part of the tube is wiped again. The cotton and yellow zone are then removed through the lower end of the tube and put into a third 100-ml. beaker.

Into each beaker is put about 25 ml. of 95 per cent ethanol to desorb the dyes. Each beaker is stirred, and the contents filtered through paper. A paper 9 cm. in diameter suffices for the victoria blue, but 12.5-cm. papers are required for the other two dyes. The filtrates and ethanolic washings are caught in graduates. The washing is continued until 50 ml. have been collected from the adsorbent with victoria blue, but 100 ml. must be collected in the other two cases to get reasonably complete recovery of the dyes. Each filtrate is then agitated and compared with a standard solution of the respective dye in a Duboscq colorimeter. The standard victoria blue should contain 100 γ in 50 ml. The other standards should contain 100 γ in 100 ml.

The results are shown in Table 1.

TABLE 1

UNCORRECTED RESULTS

Unknown Number	γ *Victoria Blue*			γ *Crystal Violet*			γ *Auramine*		
	Taken	*Found*	*Error*	*Taken*	*Found*	*Error*	*Taken*	*Found*	*Error*
1	45	64	+19	140	99	− 41	220	215	− 5
2	180	200	+20	220	185	− 35	500	378	−122
3	190	192	+ 2	170	145	− 25	70	60	− 10
4	15	65	+50	950	850	−100	30	24	− 6
5	50	52	+ 2	15	11	− 4	650	625	− 25
6	420	460	+40	140	125	− 15	300	245	− 55
7	140	169	+29	190	164	− 26	40	32	− 8
8	440	454	+14	120	99	− 21	55	52	− 3
9*	50	38	−12	460	450	− 10	190	164	− 26
10*	10	12	+ 2	270	247	− 23	490	408	− 82

* The disc of filter paper was put in the beaker with the violet adsorbent

The low results for auramine and crystal violet are probably due to incomplete desorption of these dyes by the ethanol and to decomposition of these dyes, catalyzed by the alumina. The positive errors for victoria blue require a different explanation. They are due to retention of some crystal violet by the disc of filter paper and subsequent desorption of this crystal violet along with the victoria blue. In most cases the quantity of crystal violet thus contaminating the victoria blue is too small to enable the eye to detect a change in the quality of the blue color. In numbers 1 and 4, however, where the ratio of crystal violet to victoria blue was large, a distinct violet tint was observed when the desorbed victoria blue was examined in the colorimeter. Table 1 reveals a rough correlation between the quantity of crystal violet in the unknown and the error for victoria blue.

To test the hypothesis that crystal violet is retained by the disc of filter paper, solutions 9 and 10 were prepared with a large ratio of crystal violet to victoria blue, and they were analyzed by the foregoing procedure except that the discs of filter paper were put in the beakers with the violet bands. Table 1 reveals that this modification gives good results. This modification cannot be applied unless the filter paper has a violet color, *i. e.*, unless the ratio of crystal violet to victoria blue is large.

The foregoing discussion of the nature of the errors suggests the possibility of computing approximate corrections for them. The following empirical corrections were selected. (1) It was assumed that for every 100 γ of crystal violet found (uncorrected), 7 γ of crystal violet were mixed with the victoria blue. Therefore 7 per cent of the uncorrected crystal violet found was substracted from the victoria blue found. (2) The uncorrected quantity of crystal violet found was increased by 23 per cent—7 per cent for retention by the disc of filter paper and 16 per cent for decomposition and incomplete desorption. Of course, in the modified procedure (unknowns 9 and 10) only 16 per cent was added. (3) The quantity of auramine found was increased by 16 per cent to account for incomplete

desorption and decomposition. The corrected results are given in Table 2.

TABLE 2

CORRECTED RESULTS

Unknown Number	γ Victoria Blue Taken	Found	Error	γ Crystal Violet Taken	Found	Error	γ Auramine Taken	Found	Error
1	45	57	+12	140	122	−18	220	249	+29
2	180	187	+ 7	220	227	+ 7	500	438	−62
3	190	182	− 8	170	178	+ 8	70	70	0
4	15	5	−10	950	1046	+96	30	28	− 2
5	50	51	+ 1	15	13	− 2	650	725	+75
6	420	451	+31	140	154	+14	300	284	−16
7	140	158	+18	190	202	+12	40	37	− 3
8	440	447	+ 7	120	122	+ 2	55	60	+ 5
9	50	38	−12	460	522	+62	190	190	0
10	10	12	+ 2	270	287	+17	490	473	−17

It may be concluded that the recommended procedure yields results with a relative error of ± 13 per cent or better for quantities of dyes over 90 γ and a maximum absolute error of ± 12 γ for smaller quantities.

It remains now to explain several steps in the procedure.

"Hyflo-Supercel" is added to the adsorbent to increase its porosity and thus to decrease the time required for the determination.

The chromatogram is developed with 0.002 *M* primary sodium phosphate and 0.002 *M* secondary sodium phosphate rather than with water to improve the separation. The action of the phosphate solution is not entirely a matter of buffering, for other buffers of the same pH do not have the same effect. Adsorption of the phosphate undoubtedly plays some role.

The unknowns are prepared and added in ethanolic, rather than aqueous, solution to increase their stability. Auramine is particularly unstable in water. The solutions in ethanol were stored in the dark but subjected frequently to ordinary daylight for a period of five months without decomposition. The use of ethanol as a solvent requires a rather concentrated solution of unknown lest sufficient ethanol be introduced with the unknown dye mixture to affect the chromatogram.

After the apparatus is assembled and the standard solutions prepared, the student can easily run a determination in two three-hour laboratory periods. During the first period, the chromatogram must be developed, the dyes separated, and the ethanol added to each fraction. Otherwise, if the dyes are left in contact with alumina in aqueous medium, excessive decomposition may occur. The second period is then used for the filtrations and colorimetric determinations.

What's Been Going On

(*Continued from page 102.*)

Assimilable Calcium

Calcium alpha-hydroxy-isobutyrate, marketed in borated solution as calcium "borohibate," produced commercially for the first time by the American Cyanamid Company, provides calcium in readily assimilable form.

The Platinum Metals

Palladium is finding dental use. Alloyed with gold, it is used for inlays and for partial and full dentures. Platinum itself is well established as a basis for dental porcelain work. Palladium is also used in telephone relays, and as a hydrogenation catalyst, especially for organic compounds. Platinum-rhodium alloys are in demand for rayon spinnerettes, and in the form of gauze for ammonia oxidation. In airplanes, platinum-iridium and platinum-ruthenium are used for magneto points, and may find application in spark plugs. Platinum-clad nickel is being developed for optical frames, but one of the most recent uses of platinum is in the form of leaf for exterior decoration, because of its resistance to tarnish and atmospheric discoloration. This leaf, also available for outdoor signs and for sculpture, is beaten by machine and by hand to a thickness of only one quarter-millionth of an inch.

SYMPOSIUM AT THE ST. LOUIS MEETING OF THE DIVISION OF CHEMICAL EDUCATION

AT THE meeting in St. Louis, April 7 to 10, the program of the Division of Chemical Education will include a symposium on "Reorganization of the College Chemistry Curriculum." It will deal with the work ordinarily covered in the junior and senior years, as follows:

Introduction—John C. Bailar, Jr.
Courses in Advanced Inorganic Chemistry—P. W. Selwood, Northwestern University
Discussion by J. A. Babor, College of the City of New York
Courses in the Identification of Organic Substances—R. L. Shriner, University of Illinois
Discussion by George H. Coleman, University of Iowa
Courses in Physical Chemistry—Frank Hovorka, Western Reserve University
Discussion by W. Albert Noyes, Jr., University of Rochester
Senior Research—John H. Yoe, University of Virginia
Discussion by J. L. Riebsomer, DePauw University

The success of the similar symposium at the Detroit meeting, which dealt with the curriculum of the first two college years, indicates the likelihood of a profitable and enthusiastic session.

WHAT'S IN A NAME?

Then there is the story of the man with rheumatic pains, which his doctor thought would be relieved by "nitrate of potash." The patient took the medicine for some time but was not much benefited. The doctor did not see him for some time, until one day he met him and asked after his health. "Oh, I'm getting well, doctor," was the reply, "but 'tain't your medicine. I tried that for quite a while, 'til a neighbor told me of something he took for his rheumatism. It was a very simple thing; I tried it and it did me a lot of good." "What is it?" asked the doctor. "Well, I rather hate to tell you. It's so simple you'll laugh at me. It's saltpeter."

The Coördination Theory and Coördination Compounds of the Platinum Group Metals

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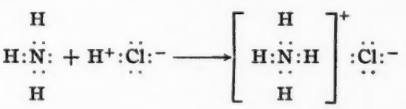
I. THE COÖRDINATION THEORY

THE coördination theory, or "complex compound" theory, first conceived by Alfred Werner in 1893 and put on an electronic basis by Sidgwick some thirty years later, has become one of the most helpful and powerful tools of the modern chemist. While it is true that the theory was originally devised to interpret the reactions and properties of the metal-ammines and similar complex salts, actually this theory finds application in everyday laboratory experience. It has served to elucidate the chemistry of some of the simplest as well as some of the most complex compounds.

Coördination compounds in the arts are of great practical and theoretical importance. The phthalocyanines, a series of deep blue pigments of remarkable stability, are coördination compounds of certain metals such as copper. Their discovery is one of the most notable of recent developments in the chemistry of synthetic coloring matters. The lakes of mordant dyes are considered to be inner metallic complexes. In many cases the extraction and purification of metals depend on the intermediate formation of coördination compounds. The successful deposition of a metallic coating from a solution of a salt depends to some extent on the type of compound used, and usually complex salts give the most satisfactory results. The coördination theory also explains the structures of many of the extremely complex minerals and of compounds in the vegetable and animal kingdoms such as chlorophyll and hemoglobin.

The Coördinate Bond

The coördinate bond or link, a vital part of the coordination theory (*1*), can be illustrated by a consideration of the simple compound ammonium chloride. The nitrogen atom contains five electrons in its outermost electron shell and can complete its octet by acquiring three electrons from three hydrogen atoms. In the resulting molecule, NH_3, the three hydrogens are held by covalent bonds; that is, a pair of electrons is shared between each hydrogen and the nitrogen atom, one of these electrons having come from the hydrogen and the other from the nitrogen. Only three of the five valence electrons of the nitrogen have been used, however, and the remaining two electrons are still available for covalent purposes. In hydrochloric acid the hydrogen atom has lost its electron to the chlorine, completing the octet of the latter. The hydrogen is now left without an electron but can acquire a helium-like structure by sharing the lone pair of available nitrogen electrons. In this event the positive charge of the proton (hydrogen ion) now resides on the resulting ammonium radical. The final product is ammonium chloride, and its formation can be represented by the following equation:



Ammonium chloride furnishes an example of each of the three types of valence: electrovalence, covalence, and coördinate valence (coördinate covalence). The chlorine is ionic and its union to the ammonium radical represents an electrovalent bond. The proton which attached itself to the nitrogen of the ammonia molecule is said to be held by a coördinate bond, and the three other hydrogens by covalent bonds. Once the ammonium radical has been formed, however, all the hydrogen-nitrogen bonds appear to be identical and it is impossible to say which was the fourth hydrogen to become attached to the nitrogen.

The coördinate link is indicated by a dotted line or, more frequently, by an arrow pointing away from the atom which contributes the shared electrons (the "donor atom") and toward the atom which accepts them (the "acceptor atom"). On this basis the ammonium radical is written $[H \leftarrow NH_3]^+$.

Coördination Number

The coördination number[2] of an atom refers to the number of groups which the atom coördinates to itself. For example, in $K_2[PtCl_4]$ and $K_2[PtCl_6]$ the coördination number of platinum is four in the former compound and six in the latter. The central atom and its coördinated groups are usually enclosed in brackets, as illustrated above, to indicate the fact that this whole complex acts as a unit and the coördinated groups are non-ionic. The coördinating groups tend to cluster about the central atom in some regular geometric pattern which is characteristic of the particular atom involved. Because of this tendency of the groups to become symmetrically situated in space, relatively few coördination numbers are actually observed. The most common ones are four and six.

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[2] Coördination number as defined here should not be confused with coördination number as used in crystal structure chemistry.

Stereoisomerism

Coördinate bonds exhibit the property of being directed in space at more or less definite angles about the central atom. This is a fundamental difference between a coördinate bond and an electrovalent bond, and because of this difference coördination compounds give rise to many interesting structural possibilities entirely absent in ionic compounds.

A unique consequence of this directional distribution of the valence forces in space is the phenomenon of stereoisomerism, or space isomerism, which implies that the isomers differ in the three-dimensional space arrangement of the atoms or groups within the molecules. Two types of stereoisomerism are optical isomerism and *cis-trans* isomerism, both of which are discussed below.

Optical Isomerism

From a purely theoretical standpoint it is possible to arrange the valence bonds about a tetracovalent atom (*i. e.*, an atom with a coördination number of four) in a variety of ways. Of these, however, only the tetrahedral and planar arrangements appear actually to exist. With a tetrahedral configuration the valence forces are directed toward the corners of a tetrahedron as illustrated in Figure 1. In the case of a planar distribution, these valence forces are directed toward the corners of a square as shown in Figure 2. Chemical methods or X-ray analysis must be resorted to in determining which of these two configurations an atom possesses.

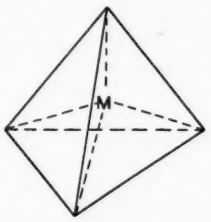

FIGURE 1

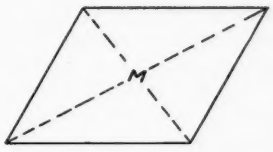

FIGURE 2

It can be shown that when the valence bonds of a tetracovalent atom having a tetrahedral configuration are satisfied by *four different groups* the phenomenon of optical isomerism is exhibited and the compound is said to be optically active. That is to say, such a compound has the power of rotating the plane of polarized light. This ability to affect polarized light apparently is associated with the fact that the structure of such a compound is without complete symmetry from a geometrical standpoint. A test for such asymmetry is whether the molecule possesses a mirror image *not* superimposable upon itself. The process of effecting the separation of two isomers bearing such a mirror-image relationship is known as "resolution."

Another way of searching for optical activity in a molecule is to determine whether or not the molecule contains a plane of symmetry, *i. e.*, whether a plane can be passed through the molecule in such a way that the half of the molecule on one side of the plane is an exact mirror-image reflection of the other half. If such a plane is present, then the molecule possesses an element of symmetry and is *not* optically active. If, however, no plane of symmetry or other element of symmetry is present, the molecule is asymmetric and can exist in enantiomorphic forms. When two or more of the groups attached to an atom with a tetrahedral structure are similar, the molecule has a plane of symmetry and does not exhibit optical activity. This becomes apparent with the aid of three-dimensional models.

Cis-Trans Isomerism

Cis-trans isomerism is encountered in the case of a planar arrangement of the four valence bonds of an atom. This type of isomerism is likewise dependent on

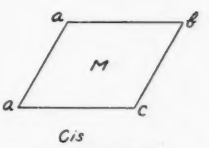

FIGURE 3

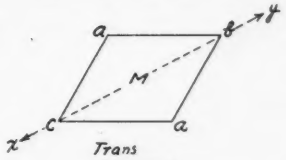

FIGURE 4

the spatial arrangement of the groups. Figure 3, in which the groups *aa* are *adjacent* to each other, represents the *cis* form, and Figure 4, in which these groups are *opposite* to each other, the *trans* form. No optical isomerism is possible with either of these molecules since each has a plane of symmetry in the plane of the four groups and the central atom, and in addition the *trans* form has a plane of symmetry along the axis *xy* perpendicular to the plane in which the atoms lie. In contrast to the tetrahedral configuration, no optical isomerism is possible with the planar arrangement even when all of the four groups are different. On the other hand, *cis-trans* isomerism is not possible in the case of the tetrahedral arrangement.

Hexacovalent atoms appear almost without exception to have an octahedral distribution of their valence bonds. That is, the six coördinated groups in a complex containing such an atom appear to adopt a symmetrical arrangement and to behave as if they were located at the six corners of an imaginary octahedron described

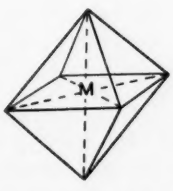

FIGURE 5

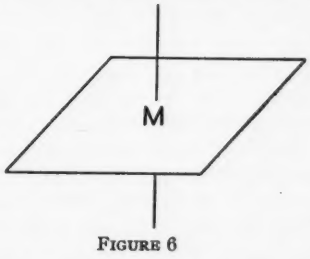

FIGURE 6

about the sphere of influence of the central atom, as indicated in Figure 5. For the sake of convenience and simplicity this diagram is usually abbreviated to that

shown in Figure 6. In compounds of this type an amazing degree of complexity is possible, since both *cis-trans* and optical isomerism may be present in the same molecule. Numerous examples of such complexes are given later.

Although the remaining discussion is devoted almost exclusively to representative coördination compounds of the platinum group metals, the coördination theory is of much wider general application. The coördination compounds of cobalt have undoubtedly received more thorough study than those of any other element. As a group, however, the platinum metals can be used most advantageously in interpreting the coördination theory.

II. COÖRDINATION COMPOUNDS OF PLATINUM

It was early recognized that platinous chloride easily enters into combination with diverse groups to form complex compounds. Thus, when ammonia is added to platinous chloride and the precipitate so formed is boiled with ammonia, a compound results having the composition $[Pt(NH_3)_4]Cl_2$. In Werner's original terminology the chlorine atoms in platinous chloride are held by "primary" valence bonds. In addition to these primary valences, the platinous atom possesses "auxiliary" or "secondary" valences which can be called upon under the proper conditions to unite with various groups, such as the ammonia molecules in the above example, and so give rise to a great variety of compounds.

Since the advent of the electronic theory of valence, Werner's terms have been largely supplanted by terms in keeping with modern nomenclature. In the compound $[Pt(NH_3)_4]Cl_2$ the ammonia molecules are considered to be directly united to the platinum atom by coördinate bonds, while the chloride ions are held by ionic or electrovalent bonds outside the complex radical. That these bonds are really fundamentally different is evidenced by the chemical reactions of the compound. The chlorine is ionic and can be completely precipitated by silver nitrate. In double decomposition reactions the ammonia molecules and the platinum together act as a stable unit with a positive charge of two. The ammonia is bound firmly and intimately to the platinum atom, as indicated by the fact that the platinum is not precipitated as a sulfide from a solution of the salt, and the usual tests for platinous ion fail.

Platinic chloride, $PtCl_4$, adds two molecules of hydrochloric acid, giving rise to the well-known acid $H_2[PtCl_6]$. In this compound the six chlorines are attached to the platinum by coördinate bonds, the chloroplatinate ion acts as a unit, and the hydrogens are ionic. Double decomposition reactions give compounds such as $K_2[PtCl_6]$ and $(NH_4)_2[PtCl_6]$. Silver nitrate gives the salt $Ag_2[PtCl_6]$ and not silver chloride.

Not only can ammonia molecules and chloride ions act as the coördinating units in such complexes, but a large number of other groups and ions can function similarly. In fact, it was soon recognized that almost any neutral or negative group having a pair of unshared electrons may act as a donor group in forming a coördinate bond with the central metal atom.

The donation of a pair of electrons by the entering group to the central atom is indicated with an arrow, as previously explained, thus: $M \leftarrow NH_3$. The valence of the resulting complex radical is determined by the nature of the entering group. If the coördinating group is neutral, no change of valence occurs, but if a negative group enters the complex a decrease in valence results. In the compound $[Pt(NH_3)_6]Cl_4$ six neutral groups (ammonia molecules) are coördinated with the platinum, and thus the resulting valence of the complex radical is plus four, the same as the valence of the platinic ion itself. If four negative groups enter the coördination sphere, as in the compound $[Pt(NH_3)_2Cl_4]$, the four positive valences of the platinum are neutralized (by the negative chloride ions) and the complex has zero valence. Conductivity experiments show this compound is actually non-ionic, as the formula indicates. If more than four negative groups coördinate with the platinum atom as, for example, in $K[Pt(NH_3)Cl_5]$ and $K_2[PtCl_6]$, not only are the positive valences of the platinic platinum neutralized, but the resultant complex radicals assume valences of minus one and minus two, respectively, as indicated by the formulas.

There are many examples of platinum compounds containing coördinated ammonia or substituted ammonia molecules, such as methylamine, pyridine, aniline, and hydroxylamine. Molecules of the type Et_2S, CO, H_2O, NO, PCl_3, $P(CH_3)_3$, and $CH_2{=}CH_2$; and ions such as NO_2^-, CN^-, Cl^-, CNS^-, and NO_3^-, all can serve as donor groups.

Some of these form unusually stable complexes with platinum. The nitro group (NO_2^-), for example, which coördinates with platinum in such a way as to form a nitrogen-metal bond rather than an oxygen-metal bond, gives rise to platinous nitro compounds stable enough to be reduced to platinous ammines without causing a rupture of the coördinate bond between the nitrogen and platinum. The term "ammine" designates the coördination compounds having ammonia coördinated to the central metal atom in the complex radical.

In addition to the groups united by one point of attachment there are numerous molecules and radicals possessing two points of attachment to the central platinum atom in the complex. Such groups are ethylenediamine (en), propylenediamine (pn), 2,2′-dipyridyl (dipy), $CO_3^=$, $SO_3^=$, $SO_4^=$, and acetylacetone, and are known as chelate groups (Greek *chele*, a crab's claw). If the donor group is capable of forming a four-, five-, or six-membered chelate ring with the central atom, the resulting union is usually very stable.

A few compounds are also known which fill three positions (tridentate groups) or even four (quadridentate groups) in the coördination sphere; 2,2′,2″-tripyridyl and α,β,γ-triaminopropane may be cited as examples of the former and β,β',β''-triaminotriethylamine and 2,2′,2″,2‴-tetrapyridyl of the latter. Tridentate and quadridentate compounds of bivalent

platinum are illustrated by Figures 7 and 8, respectively.

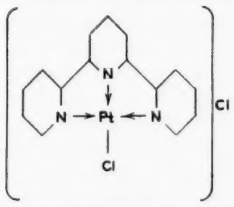

FIGURE 7

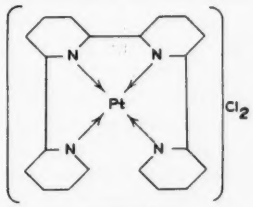

FIGURE 8

Halogen atoms, in particular, are capable of acting also as bridging units in compounds of the general formula $[PtCl_2 \cdot X]_2$. In these compounds X may be CO, PCl_3, PR_3, $P(OR)_3$, AsR_3, and $CH_2=CH_2$. (R indicates alkyl groups.)

The cyano derivatives of platinum, a series of coördination compounds, are numerous and of great complexity. The platinous compounds of the general formula $M_2^{+1}[Pt(CN)_4]$ are interesting, since many members of this class exhibit intense fluorescence under the influence of ultra-violet light and other radiations.

Bivalent platinum belongs to the group of metals which forms the important class of compounds known as metallic phthalocyanines (*2*). These compounds, particularly those of copper, are becoming increasingly important in the pigment field. The development of these substances has been termed the most significant advancement in the inorganic pigment field during the last one hundred years. These pigments are all blues or greens, of high tinctorial strength, and many are brilliant in shade. They are unusually stable toward heat and chemical agents and remain virtually unchanged by long exposure to the atmosphere. Due to their many desirable properties these substances are finding application in all fields in which colored pigments can be used. While these compounds can be made to assume great complexity, they are all characterized by the unusual 16-membered ring skeleton shown in Figure 9. The ease with which this large ring forms is remarkable. The two hydrogen atoms attached to nitrogen can be replaced by various metal ions to give the metallic phthalocyanine pigments. In these substances the metal is coördinated with four or more of the nitrogens, depending on the coördination number of the metal.

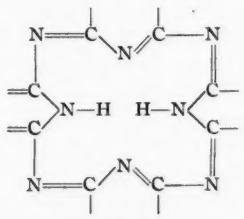

FIGURE 9

A very interesting class of compounds known as "carbonyls" results from the reaction of carbon monoxide with derivatives of platinum and some of the other platinum group metals. In these substances the carbon monoxide molecule acts as a donor group, coördination occurring through the carbon atom. One of the best known of the platinum carbonyls is the compound $[OC \rightarrow PtCl_2]$, which is stable enough to be distilled without decomposition. Since only three associating units are present in the coördination sphere, this platinous compound may be regarded as unsaturated. Due perhaps to this unsaturated character, hydrogen chloride combines directly with the carbonyl, giving rise to an acid of the type $H[PtCl_3 \cdot CO]$. This acid is very unstable, but a number of salts have been obtained as crystalline compounds.

The above platinous carbonyl is probably a dimeric compound in which two chlorine atoms act as bridging units between the platinum atoms. On this basis, there are three possible arrangements of the CO molecules, as shown by Figure 10.

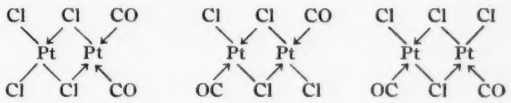

FIGURE 10

The coördination compound ammonium chloroplatinate, $(NH_4)_2[PtCl_6]$, is an important intermediate in the isolation of platinum and in its estimation. This compound, on ignition, easily decomposes to form spongy platinum.

The use of dithio-oxamide, which gives a blue or violet precipitate with nickel salts, has been extended to the quantitative precipitation of platinic salts. The compound formed is shown in Figure 11.

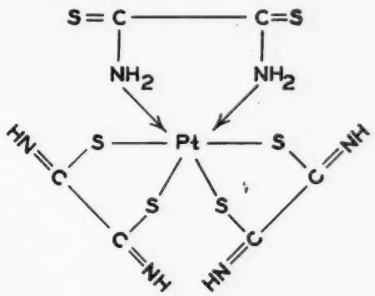

FIGURE 11

The electrodeposition of platinum has presented considerable difficulty, because it is impossible to use the metal as a soluble anode for continuous deposition. It has been found feasible, however, to successfully plate platinum from the non-ionic coördination compound $[Pt(NH_3)_2(NO_2)_2]$ in a solution containing certain ionic compounds. Platinum has also been deposited from a hot solution containing the coördination compound sodium chloroplatinate, $Na_2[PtCl_6]$, and sodium and ammonium phosphates.

Stereoisomerism Among the Coördination Compounds of Platinum

Platinous Platinum.—In the great majority of platinous complexes the platinum atom has a coördination number of four. As early as 1893 Werner proposed a planar arrangement of these four valence bonds about the platinum. This seemed justified from a study of a number of these tetracovalent compounds. His idea was subsequently challenged and only recently has additional evidence seemed to justify completely Werner's original interpretation.

One of the most ingenious and convincing proofs of the planar arrangement of the groups about the platinous atom was furnished by Mills and Quibell (*3*), who succeeded in resolving the bis-chelate compound meso-stilbenediamino-isobutylenediamino-platinous chloride, the cation of which is shown in Figure 12. If the four valence bonds of the platinum atom lie in one plane, then the two rings in this cation are coplanar and the compound will have no element of symmetry; that is, the molecule will be optically active. If, on the other

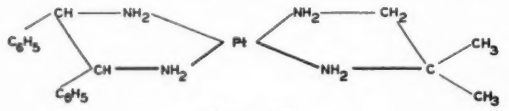

FIGURE 12

hand, the valences are arranged tetrahedrally, the chelate rings lie in planes perpendicular to one another and a plane of symmetry is present. Since resolution was effected, a coplanar distribution is indicated. X-ray evidence also supports this view. The nitrogen atoms in the compounds $[Pt(NH_3)_4]Cl_2 \cdot H_2O$ and $[Pt(en)_2]Cl_2$ were shown by X-ray studies to lie in the same plane as the platinum atoms.

This planar arrangement of the four groups about the platinum gives rise to *cis-trans* isomerism. Such isomerism is evidenced by the non-ionic compound $[Pt(NH_3)_2Cl_2]$. The *cis* and *trans* forms of this molecule are illustrated in Figure 13. These two compounds differ in physical and chemical properties but are not optically active.

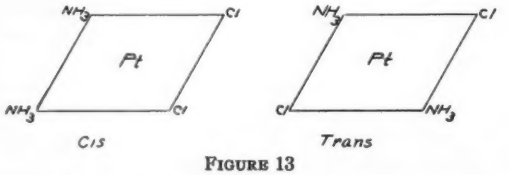

FIGURE 13

The fact that trimethylplatinic chloride, $[Pt(CH_3)_3Cl]$, a tetracovalent compound of quadrivalent platinum, has been shown to be non-planar and is most probably tetrahedral is of unusual interest. This indicates that a change in the primary valence of the platinum is a factor of importance in deciding the configuration of its four-covalent derivatives.

It seems certain that bivalent platinum is also hexacovalent in some compounds.

Platinic Platinum.—The usual coördination number of platinum in platinic complexes is six. In keeping with the general rule concerning hexacovalent atoms, platinic platinum has an octahedral distribution of its valence bonds. The spatial arrangement of the coördinating groups in $[Pt(NH_3)_6]Cl_4$ is shown in Figure 14. In such a compound all the ammonia molecules are symmetrically situated about the platinum atom, and the complex possesses a point of symmetry and numerous planes of symmetry; consequently no type

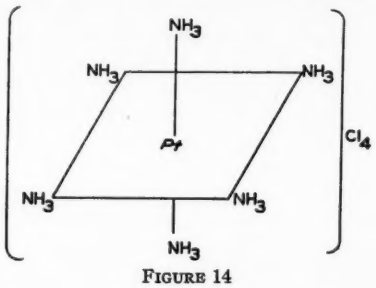

FIGURE 14

of isomerism is possible. However, in the compound $[Pt(NH_3)_4Cl_2]Cl_2$, *cis-trans* isomerism is possible but not optical isomerism, since elements of symmetry are present. The *cis* and *trans* forms (Figure 15) differ in both their physical and chemical properties. In the *cis* form the chlorines are *adjacent*, whereas in the *trans* form they are *opposite* or *across* from one another.

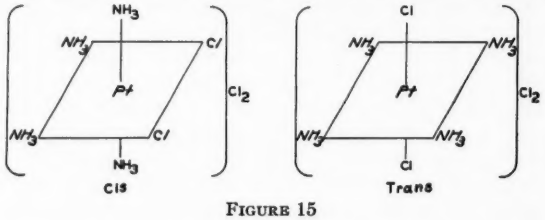

FIGURE 15

With the compound $[Pt(en)_2Cl_2]Cl_2$, both *cis-trans* and optical isomerism are possible (en = ethylenediamine, $H_2N—CH_2CH_2—NH_2$). Figure 16 illustrates

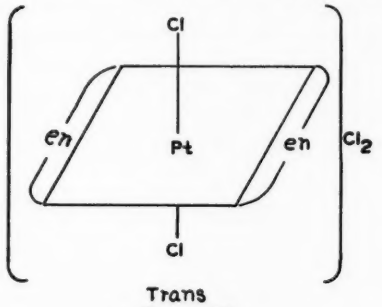

FIGURE 16

the *trans* form, which is not optically active because planes of symmetry are present. The *cis* form, however, possesses no element of symmetry and can therefore exist in two non-identical forms which bear a

mirror-image relationship to each other (Figure 17). One is termed the *dextro* form and the other the *levo*. These forms are similar in all their chemical and physical properties except the direction in which they rotate plane polarized light.

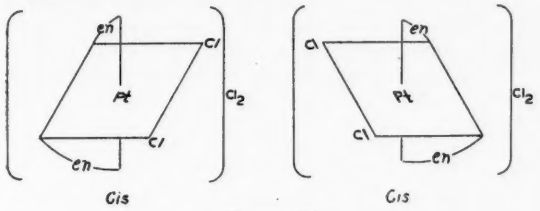

FIGURE 17

It is apparent from the above figures that the amino groups in the ethylenediamine molecule occupy *adjacent* positions in the coördination sphere in both the *cis* and *trans* configurations. Inasmuch as all bidentate groups act similarly in this respect, it appears that these molecules are not able to span the *trans* positions.

III. COÖRDINATION COMPOUNDS OF THE OTHER PLATINUM METALS

Even a casual survey of the compounds of the platinum group metals reveals that coördination plays a predominant part in the chemistry of these substances. From a consideration of the position of these metals in the periodic table it might well be supposed that much which has been said concerning the chemistry of platinum applies equally well to the other platinum metals. This in general is the case.

General Group Relationships

Of this group, ruthenium and osmium furnish hexacyano compounds of the type $K_4[Ru(CN)_6]$ and $K_4[Os(CN)_6]$. Rhodium and iridium are distinguished by forming anionic complexes of the type $K_3[M^{+3}(NO_2)_6]$ and ammines of the general formula $[M^{+3}(NH_3)_6]Cl_3$. These latter compounds are analogous to the corresponding cobaltic ammines, but there appears to be a marked fading out of color with increase in the atomic weight of the central metal. Both palladium and platinum form complexes of the type $K_2[M^{+2}(CN)_4]$.

The general family relationship of the Group Eight metals is well illustrated by the similarity in properties and the many examples of isomorphism of their coordination compounds. The tetracyano compounds of palladium and platinum mentioned above form isomorphous crystals. Similarly, the hydrated hexacyano complexes of ruthenium and osmium are isomorphous with the well-known compound potassium ferrocyanide, $K_4[Fe(CN)_6]\cdot 3H_2O$, but neither ruthenium nor osmium forms compounds analogous to the ferricyanides. The hexacyano compounds of iridium and rhodium, however, are isomorphous with the corresponding cobaltic and ferric compounds, such as potassium ferricyanide, $K_3[Fe(CN)_6]$. The complexes $K_2[IrX_6]$ are well defined and are isomorphous with the corresponding platinic derivatives $K_2[PtX_6]$. (X = Cl, Br, I.)

Compounds of Palladium

The compounds of palladium resemble those of platinum more closely than they resemble the compounds of any other member of the group. Palladium, like the other metals of the platinum family, has a marked ability to form coördination compounds with bases, sulfides, and other groups, and in recent years a large amount of work has been done in determining the structures of these complex compounds.

Like platinum, palladium has been shown by X-ray methods to give planar configurations in certain of its four-covalent compounds. Also, the extremely clever method employed in proving the planar configuration of bivalent platinum has now been used successfully by Lidstone and Mills (*4*) to prove a similar configuration for bivalent palladium. There now appears to be little doubt that the planar configuration is quite general for four-covalent compounds of bivalent palladium and that it can only be modified in very special cases such as may arise with tri- or quadridentate groups.

Ammonia reacts with palladous salts, producing two series of coördination compounds whose general formulas are as follows: $[Pd(NH_3)_2X_2]$ and $[Pd(NH_3)_4]X_2$. Several ammine derivatives of palladic salts have been reported but these are very unstable. Somewhat more stable coördination compounds result when pyridine is substituted for ammonia.

Palladous chloride, $PdCl_2$, has been studied by Wells (*5*), who has shown by crystallographic investigation that the compound consists of long chains of palladium atoms bridged by chlorine atoms (Figure 18). The $PdCl_2$ units are united through a series of coördinate linkages which may be continued indefinitely.

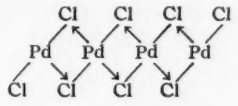

FIGURE 18

Palladium forms a compound with 2,2′,2″-tripyridyl similar in character to that formed by platinum (Figure 7).

Compounds of Iridium

Complex derivatives containing trivalent iridium resemble in a general way the corresponding salts of rhodium and cobalt. This might be anticipated since the Co^{+3}, Rh^{+3}, and Ir^{+3} ions require twelve electrons each to attain the effective atomic numbers of the next higher inert gases—krypton, xenon, and radon, respectively.

Many well-defined coördination compounds are known in which trivalent iridium is present in complex anions or cations, as, for example, $K_3[IrCl_6]$ and $[Ir(en)_3](NO_3)_3$. Figure 19 illustrates in simplified form a compound in which a quadridentate molecule, 2,2′-

2″,2′″-tetrapyridyl, is coördinated with trivalent iridium.

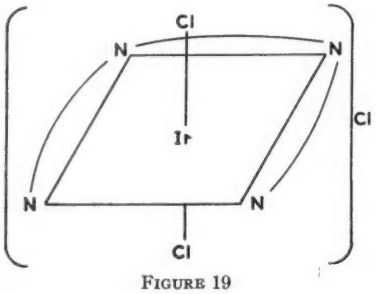

FIGURE 19

The deep violet colors of the ammines of tetravalent iridium, that of the complex $[IrCl_2(NH_3)_4]Cl_2$ in particular, are in distinct contrast to the colorless trivalent ammines such as $[IrCl_2(NH_3)_4]Cl$.

Compounds of Rhodium

The similarity of rhodium and cobalt is particularly well illustrated by the many examples of stable rhodammines analogous to the cobaltammines. Of these the best known are the luteo series $[Rh(NH_3)_6]X_3$ (hexammine), roseo series $[Rh(NH_3)_5H_2O]X_3$ (aquopentammine), and purpureo series $[Rh(NH_3)_5X]X_2$ (pentammine). It is interesting to note, however, that unlike the corresponding cobalt compounds the hexammine rhodium salts are colorless.

Molecular asymmetry among purely inorganic compounds is very rare; therefore, it is noteworthy that the rhodium compound $Na[Rh(NHSO_2NH)_2(H_2O)_2]$ is the second of only two such compounds which have thus far been resolved (*6*). This compound contains two four-membered chelate rings devoid of carbon and the *cis* forms possess a mirror-image relationship as shown by Figure 20.

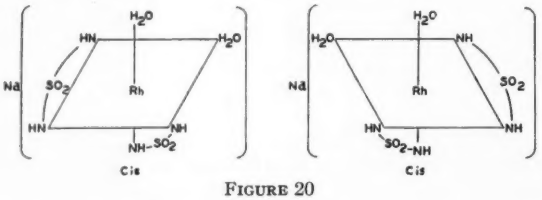

FIGURE 20

Compounds of Osmium and Ruthenium

Osmium is the only metal of the platinum group which unites readily with oxygen. The product of the oxidation, $[OsO_4]$, is perhaps the best known and most important compound of osmium. The structure of this poisonous oxide is best represented by the formula indicated in Figure 21, which is in satisfactory agreement with its chemical and physical properties. Osmium and ruthenium are the only members of Group Eight which form oxides of this type, although the position of the Group Eight metals in the periodic table would lead to the conclusion that this should be the common oxide.

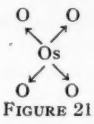

FIGURE 21

Both ruthenium and osmium form compounds with the tridentate molecule 2,2′,2″-tripyridyl. A tripyridyl complex of bivalent osmium is shown in Figure 22. It is interesting to note in this connection that

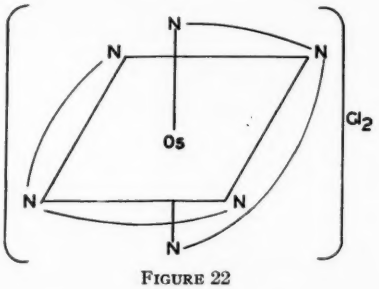

FIGURE 22

other spatial arrangements of the two tridentate molecules are possible; as a result, six isomers of this complex are theoretically possible.

An interesting example of a four-covalent atom is osmium in the osmiamates, $M^{+1}[OsO_3N]$. The osmiamate ion, $[OsO_3N]^-$, has recently been shown (*7*) to be very nearly tetrahedral, and a structure for this ion has been proposed in which the nitrogen atom carries the negative charge:

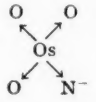

FIGURE 23

Ruthenium forms coördination compounds with ammonia which are analogous to the well-known cobalt and chromium ammines, but the hexammines of ruthenium are colorless like those of rhodium.

An interesting coördination compound containing trivalent ruthenium in the cation is $[Ru(NH_3)_4(OH)Cl]Cl$. This is an intensely colored salt and commonly called "ruthenium red" because of its capacity for dyeing natural silk in purplish red shades.

Dipyridyl forms with bivalent ruthenium a remarkably stable series of coördination compounds having the formula $[Ru(dipy)_3]X_2 \cdot yH_2O$. These compounds can be boiled with fifty per cent potassium hydroxide without destruction of the complex.

Red and green forms of the acid $H[RuCl_4(H_2O)_2]$ have been obtained. These two forms apparently are *cis* and *trans* isomers.

Carbonyls

Numerous carbonyls of the platinum group metals are known. Ruthenium forms three well-defined carbonyls, $[Ru(CO)_2]$, $[Ru(CO)_5]$, and $[Ru_3(CO)_9]$, and carbonyl halides of the type $[RuX_2(CO)_2]$. Palladium

also gives rise to several carbonyl derivatives. Of these the compound $[PdCl_2 \cdot CO]$ resembles the corresponding platinum compound in that it dissolves in hydrochloric acid, forming the unstable acid $H[PdCl_3 \cdot CO]$. Carbonyls of the other platinum metals also have been reported.

Stabilization of Valence States by Coördination

In general, carbon monoxide tends to combine with the metals of the eighth group in their lower states of valence and in some cases there is a marked tendency for a lower valence state to become stabilized by the coördinated carbon monoxide molecule. An example of this is univalent ruthenium in the compound $[OC \rightarrow RuBr]$. A more familiar example of a carbon monoxide complex is $[CuCl \cdot CO] \cdot 2H_2O$, which results when cuprous chloride, dissolved in either hydrochloric acid or ammonia, is brought into contact with carbon monoxide. Cuprous chloride has long served in gas analysis because of its absorptive power for carbon monoxide.

Stabilization of a valence state by coördinated carbon monoxide molecules is only a specific example of a rather general phenomenon among coördination compounds. There are many instances in which an otherwise unstable valence may become stabilized by coördination. This is particularly well illustrated by tetravalent palladium. Simple palladium salts of this valence state are practically unknown, yet there is a well-defined series of salts of the type $M_2^{+1}[PdCl_6]$. This generalization also applies to trivalent iridium and trivalent osmium. Although a few simple salts of trivalent iridium are known, most of the best defined compounds exhibiting this valence are the coördination compounds in which iridium is present in complex anions or cations, as in the compounds $K_3[Ir(NO_2)_6]$ and $[Ir(NH_3)_6]Cl_3$. Similarly there are many examples of stable coördination compounds of trivalent osmium. Practically the sole example of a binary compound of hexavalent osmium is the fluoride $[OsF_6]$. However, alkali osmates, $M_2^{+1}[OsO_4]$, and osmyl derivatives, $M_2^{+1}[OsO_2X_4]$, are readily obtained.

Nitrosyls

The "nitrosyls" comprise another very interesting group of coördination compounds. In these compounds nitric oxide is a donor molecule with coördination occurring through the nitrogen atom. Research on these compounds seems to indicate that the metals in Group Eight having the greatest affinity for nitric oxide are cobalt, nickel, and iron and its homologs—ruthenium and osmium. The iron compound $Na_2[ON \rightarrow Fe(CN)_5]$, commonly known as sodium nitroprusside, is perhaps the best known of the nitrosyl complexes. With alkaline sulfides this compound develops an intense violet color often used as a delicate test for sulfide ion. Ruthenium reveals its close analogy to iron in the production of $Na_2[ON \rightarrow Ru(CN)_5]$, which develops a red color with sulfides. The nitrosyl derivatives of osmium having the general formula $M_2^{+1}[ON \rightarrow OsX_5]$ are isomorphous with the corresponding ruthenium salts and are remarkably stable substances. Other nitrosyl compounds of the platinum metals include $[Ru(NO)_4]$, $[Ru(NO)_6]$, $[RuBr_2 \cdot NO]$, and $[PdCl_2(NO)_2]$.

Coördination Compounds in Quantitative Analysis

A considerable amount of research has been undertaken with the hope of discovering for each metallic element a characteristic coördination compound which, by its color or insolubility, may serve to identify and quantitatively estimate the element even when present in mixtures. This, admittedly, is an ideal very difficult of realization. Nevertheless, some progress in this direction has been made with the platinum group metals. Dithio-oxamide, which has already been referred to as a reagent for tetravalent platinum, forms an insoluble coördination compound with divalent palladium and is useful in the quantitative determination of this element. Ruthenium furnishes the characteristic red compound $[Ru(OH)Cl_4(NH_3)]Cl \cdot H_2O$ with ammonia, and the stable orange salt $[Ru(dipy)_3]Cl_2 \cdot 6H_2O$ with 2,2′-dipyridyl. Osmium forms a red thiourea complex salt $[Os\{SC(NH_2)_2\}_6]Cl_3OH$. This is a rather sensitive test for osmium, the red color being perceptible at one part in 100,000. The rhodium salts $K_3[Rh(NO_2)_6]$ and $[RhCl_5(NH_3)]Cl_2$ are only slightly soluble and are frequently used in the determination of rhodium. The iridium complex $(NH_4)_2[IrCl_6]$ is sparingly soluble like the analogous platinum compound. Palladium forms insoluble coördination compounds with dimethylglyoxime and α-nitroso-β-naphthol. The structures of these compounds are shown in Figures 24 and 25, respectively.

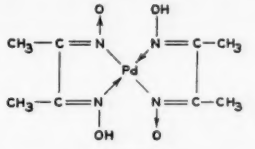

FIGURE 24

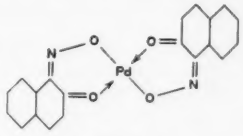

FIGURE 25

Coördination Compounds in Metallurgy

Coördination compounds are of major importance in the metallurgy of the platinum group metals. These compounds include the volatile oxides of ruthenium and osmium, $[RuO_4]$ and $[OsO_4]$, and the salts $(NH_4)_2[PtCl_6]$, $(NH_4)_2[IrCl_6]$, $K_3[Rh(SO_4)_3]$, and $[PdCl_2(NH_3)_2]$. All of these are important intermediates in the isolation of the respective heavy metals.

Coördination Compounds in Electroplating

Rhodium, which recently has attracted considerable attention as a plating element, may be deposited from sulfate and phosphate solutions, or mixtures of these, and from solutions of the chloro compound $Na_3[RhCl_6]$. Palladium is deposited from an electrolyte containing the coördination compound $[Pd(NH_3)_2(NO_2)_2]$. This compound is analogous to the complex used for the electrodeposition of platinum.

The art of electrodepositing thin films of rhodium (*8*) has become very important due to the many desirable properties of rhodium surfaces. Not only do these films show exceptional adhesion to the supporting material but they are extremely hard and possess a remarkably high reflecting power. Rhodium is said to be the only metal which retains its reflectivity unimpaired for any length of time under atmospheric conditions. Because of these properties rhodium is used for surfacing reflectors for floodlights and searchlights and for the preparation of mirrors in scientific apparatus.

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GLEANINGS FROM A CONFERENCE

FOLLOWING are some of the comments made at the round table discussion on The Modern Chemistry Curriculum, held at the National Chemical Exposition recently in Chicago. A considerable number of representatives from industry and the universities took part. These remarks have not been edited to ensure either continuity or consistency. If the shoe fits, wear it.

Failure in an industrial organization is seldom due to technical weakness, but much more often to personal eccentricities and ability to "fit in." A surprising number fail from simple inability to write and speak English adequately.

In judging of "personality" one organization reports that the rule followed is: Take his chemistry away from him and see what he has left.

"Misfits" stand a better chance of being successfully absorbed in the larger organizations.

New applicants should be passed upon by the group with which they will work, rather than merely by a personnel officer.

A conscious effort should be made to make our graduates not only competent in their chosen fields but also potential leaders in whatever fields they may finally enter. In other words, an effort at personality development.

Graduates, somewhere in their training, should be given a proper appreciation or description of the many applications of chemistry to the various specialized branches of industry, medicine, and agriculture, in order to help them choose their particular life work and avoid aimless efforts in several directions.

The first quality looked for in an applicant is *character*, which includes: alertness, enthusiasm, initiative, imagination, ambition, industry, loyalty, logic, and judgment.

A badly needed quality, which comes by inheritance rather than training, is imagination. Without it a research man is merely a pair of hands.

The most difficult thing to get young people to do is to tell what they are doing; to "sell" their work to others.

Desirable as it may be, we have no right to *expect* the chemist to be a salesman. Chemists in a research laboratory do not, in fact, need to be salesmen, but do need to have enthusiasm, tempered by cold logic and facts. Only the director, who sells the management, needs that extra qualification.

We try to crowd the chemist with too many things. When industry wants a specialist the man must be picked to fit the job. It is then the responsibility of the organization to round the man out to meet the demands made upon him.

Many graduates lack ability to study and interpret their data, and often have not been taught how. It should be part of their training to write reports on data they collect.

In addition to general training, however, some organizations have their own special methods of reporting, which they teach their own men.

There is reported a general lack of ability to think and an overemphasis on memory of the questions and answers.

Companies which have had little to do with research tend to look for men who have experience in that particular field. Slowly, however, they are convinced that it is better to get men who know fundamentals.

We need physical chemists who are better trained in organic chemistry and organic chemists better trained in physical chemistry.

The "Ph.D." has often been kept too long on the nursing bottle. He may have been kept under the professor's wing, rather than allowed to spread his own. He often expects to be fed with ideas, and in industry this is impossible.

The college man is not necessarily an *educated* man. Home and cultural backgrounds of students have changed and the science of chemistry has grown so much that the ability to read and write good English has waned, its place having been taken by more chemistry, physics, and mathematics. The larger organizations must further the education of the men they hire, perhaps by seminars and contact with experienced technical men. (One large company reported doing this.)

In answer to the question whether the M.S. degree has any value or standing, the opinion was expressed that it was a definite help and was "worth" twenty-five to thirty dollars a month to the holder.

CHEMICAL ENGINEERS NEEDED FOR NATIONAL DEFENSE WORK

QUALIFIED persons are urged by the United States Civil Service Commission to file their applications for the position of chemical engineer. Applications will be rated as received at the Commission's Washington office until further notice.

High-School Chemistry

The Future of Chemistry as a Specialized Science in the High-School Curriculum

T. A. NELSON

Decatur High School, Decatur, Illinois

I SHALL interpret specialized chemistry to be a technical course of study in chemistry designed for the student who is primarily interested in preparing himself for future work in some field of science.

High-school chemistry courses may be grouped in three classes:

(1) Technical courses, which emphasize basic fundamentals, facts, theory, etc., designed for the future science specialist.

(2) Semitechnical courses, which attempt to serve in a dual capacity to meet the needs of general education for the non-specialist and to prepare the student who is to become the future science specialist.

(3) Non-technical courses designed for general education, with no claim to preparation for future science specialization, intended for the student who terminates his formal education upon leaving high school.

Since chemistry is only one of several sciences offered in high school, it may be of some benefit to ask to what extent high-school students are enrolling in science courses and especially in chemistry. A picture of the past trends is available in the "Biennial Survey of Education,"[1] which shows a sharp decrease in the per cent of the high-school population enrolled in physics, botany, and zoölogy, a slight decrease in chemistry and general science, and a marked increase in biology. This may imply some trend toward greater popularity of generalized courses. The total enrollment in chemistry has not decreased to any appreciable extent in the last ten years, but the percentage of the school population taking chemistry has decreased.

Formerly the bulk of the program of studies was composed of academic courses designed to lay emphasis on college preparation. Today the emphasis is on meeting the needs of boys and girls in order more nearly to prepare them for the future. The data given by Anibal and Leighton[2] give one reason for the change of emphasis. Out of each 100 graduating from high school, about 35 enter institutions of higher learning. Of these 35, fewer than ten will elect to specialize in professional fields that require physics and chemistry, and of these ten only two will be graduated in those fields. The Biennial Survey of Education[3] gives these data: "It is estimated that in 1936 there were in the United States 2,257,200 living college graduates, (3.32 per cent of the adult population). In 1936 only 15.7 per cent of the population over 21 had graduated from high school." In view of this, if the secondary schools are to educate boys and girls for better participation in a democracy, they cannot justify specialized courses, designed for college preparation, and still hope to make much progress in meeting the educational needs of high-school students.

The people as a whole are far from scientific. Our gullibility with respect to radio advertising and simple propaganda, our inability to recognize authority, or to learn to seek for authoritative sources of information, are just a few of the indictments that hold us unscientific. The development of a few good scientists who have been able to solve our problems and extend our scientific knowledge has not given us a people capable of utilizing fully the fruits of science. The type of thinking used by the scientist is a necessary tool for the masses of our people if we are at all interested in preserving and perpetuating our American civilization.

The secondary schools are becoming less concerned about the content to be covered and the courses to be taken, and more concerned in meeting the personal, social, and economic needs of students and developing in them those desirable attitudes that make for a better life. What are these needs that we hear so much about? H. Emmett Brown[4] gives this rather complete list:

1. Need for a rational world-picture
2. Need for a workable philosophy of life
3. Need derived from the individual's participation in society, such as the economic and social effects of man's use of resources
4. Need for the individual to understand his own physiological functions to the end that mental and physical health may result
5. Need for self-assurance
6. Need for self-expression
7. Need for social participation
8. Need for growth of self in creativeness, personal interests, and esthetic appreciation
9. Need for effective social participation in order to develop tolerance, social sensitivity, and coöperativeness

[1] "Biennial survey of education," U. S. Department of Interior, Office of Education, **1934–36,** Vol. II, p. 20.

[2] ANIBAL AND LEIGHTON, "A plan to eliminate the overlapping in high-school and college science courses," J. CHEM. EDUC., **13,** 437–42 (1936).

[3] "Biennial survey of education," *loc. cit.*, pp. 38–9.

[4] BROWN, "The development of a course in the physical sciences for the Lincoln School," Bureau of Publications, Teachers College, Columbia University, New York City, **1939,** pp. 26–8.

10. Need for the use of intelligence in reflective thinking, for readiness to act on the basis of tentative judgment, and for self direction
11. Need for vocational guidance

Should we accept these needs as desirable for the education of boys and girls, no particular content will be favored in the curriculum. Content of some kind must be used, it is true, and science is in a position to meet some of these needs in a most satisfactory way. For example, reflective thinking, suspended judgment, tolerance, world-picture, social sensitivity, coöperativeness, etc., come directly into the field of science.

The implications for the value of science in education are more numerous than ever before. Educators are thinking in terms of unified science courses and a continuous science sequence for the elementary, junior high, and senior high schools. The present movement was preceded by the organization of biology and general science. Now we find that courses in fused physical science are being organized.

There is also a rapid revision of science textbooks. The new books that have appeared on the market within the last two years reveal an entirely new point of view. One finds the authors emphasizing the treatment of practical applications of chemistry; appreciation of the great service of chemistry to mankind; ability to think creatively in the field of chemistry; opportunity for students to develop scientific attitudes and scientific methods of attacking and solving problems; ability to understand and control our environment, etc.

All of these new and revised textbooks will not assure different courses in chemistry in our high schools. No course will be any better than the teacher who teaches it. A teacher using a new text with an entirely new emphasis does not guarantee desirable outcomes. The new textbook is a product of the thinking of the authors. A teacher, to use this textbook successfully, must follow the same thinking the author uses in order to get the correct point of view. The problem, then, is not entirely confined to textbook revision, but applies in a far greater measure to teacher education.

Investigations show that a variety of courses in chemistry and physical science have been organized in our high schools for the benefit of students who will not seek higher education. Some of these are: applied chemistry, household chemistry, visualized chemistry, descriptive chemistry, chemistry in use, functional chemistry, everyday chemistry, consumer chemistry, senior science, consumer science, and physical science.

The inability to adapt technical courses to certain groups of students in high school has undoubtedly brought about the organization of these courses. Through the courtesy of book companies I was able to learn that senior science is being offered in 702 schools in 42 states.[5] "Consumer Science"[6] came off the press last spring and has received 68 adoptions in 10 states. "Our Physical World,"[7] a textbook for fused physical science, has been on the market for two years and is being used in 113 schools in 29 states. This textbook likewise enjoys two state adoptions. This number of schools is comparatively small when compared to the large number of high schools in the United States but I believe the organization of such courses shows a slow but definite trend toward fused physical science courses for the non-college students.

In order to get additional information regarding such courses an inquiry was sent to the State Departments of Education of each of the 48 states. The replies indicated:

(1) There has been a slow but definite trend toward the organization of fused physical science courses.

(2) Chemistry enrollment has increased, but the percentage of the high-school population enrolled in chemistry has decreased.

(3) Fused physical science courses have been added to the science offerings of the larger schools but are tending to replace chemistry and physics in the smaller schools.

The continuous science program that is being considered by science supervisors in the public schools calls for elementary science in grades one through six, and a three-year general science program for grades seven, eight, and nine. In the high school, general biology will be taught in the tenth year and general physical science in the eleventh year. This program would terminate the science education for the non-college student. College preparatory students may have the choice, after the tenth year, of electing physics and chemistry in grades 11 and 12, or electing physical science in grade 11 and physics or chemistry in grade 12. Such a science program attempts to delay specialization in any one specific science until a broad background of the field of science has been attained. This is in keeping with the desire to present the field of science as a well-organized whole. Should the public schools adopt a continuous science program, courses in specialized chemistry have a doubtful future.

[5] Data collected in January, 1940.

[6] HAUSRATH AND HARMS, "Consumer science," The Macmillan Co., New York City, 1939.

[7] ECKELS AND OTHERS, "Our physical world," B. H. Sanborn Co., Chicago, Boston, 1938.

ALL IS NOT GOLD THAT GLITTERS

A verdant-looking Vermonter appeared at the office of a chemist with a large bundle in a yellow bandanna, and opening it, exclaimed: "There, doc, look at that." "Well," said the doctor, "I see it." "What do you call that, doctor?" "I call it iron pyrites." "What, isn't that gold?" "No," said the doctor, and putting some over the fire, it evaporated up the chimney. "Well," said the poor fellow finally, with a woe-begone look, "there's a widow woman up in our town has a whole hill of that, and I've been and married her."

—From *The Boston Journal of Chemistry*, 1871

LETTERS

Local Gas-Volume Relationships

To the Editor:

I wish to submit a few comments as to the desirability of giving a local meaning to gas-volume relationships and local values to supplement those normally given only for standard conditions.

The "standard conditions" that are used in connection with gas volumes are possible of exact experimental attainment in but few laboratories anywhere in the world. An air pressure exactly equal to 760 mm. of mercury is not of common occurrence even at sea level and a latitude of 53.5°N. (or halfway up the coast of Labrador), though the Weather Bureau records indicate that a year-round average of that pressure could be expected for such a location. Nor is a temperature of 0°C. a usual or a comfortable one in any laboratory. One could argue, therefore, that the standards that have been chosen are essentially impractical for either laboratory or industrial conditions.

Though one may doubt the desirability of setting up new standards that would have some measure of practicality, it is within the range of easy accomplishment for any school or any industrial establishment to translate such a volume as 22.4 liters or a hydrogen density of 0.09 grams to the corresponding volume or density that each would have under the average year-round pressure for that community and for some temperature possible of easy attainment. For most laboratories a temperature close to 20°C. (68°F.) is maintained throughout a major portion of the year; such a temperature would, therefore, be a desirable temperature standard for such laboratories.

Under such local conditions as those described the gram molecular volume will be larger than 22.4, often more than ten per cent larger. Out here at the base of the Rockies the volume at our average air pressure and for 20°C. is equal to 28.77 liters—or 28 per cent larger than 22.4 liters. For a gas collected over water the volume becomes 29.56 liters—or 32 per cent larger. We consider it desirable for our classes to calculate such values for our conditions. In quantitative work involving the collection of gases over water the student in general chemistry is permitted to use 29.56 liters as the volume of a gram molecular weight of the gas, without correction for such minor variations of pressure and temperature as may exist; the failure to make such corrections introduces an error that is commonly no greater than 0.5 per cent. The saving of laboratory time, ordinarily spent in making the calculations related to gas-volume corrections, is tremendous in the aggregate. The omission of such calculations serves to focus attention upon the weight-volume relationships of the chemical reaction.

K. Gordon Irwin

Colorado State College
Fort Collins, Colorado

Atomic Weight Unit

To the Editor:

In my first semester of teaching, I was impelled by student reaction, or lack of it, to use a name for the atomic weight unit. The students themselves suggested and adopted the terms "hep" and "pip" in two classes. One examination question read, "If an oxygen atom weighs 24 "xyzts," what does a carbon atom weigh?" The answer was almost unanimously 18 "xyzts," not 18. Students want the unit!

But why use a meaningless word, such as "pel?" I suggest the derived term "*atwu*" (pronounced at'woo), which stands for *AT*omic *W*eight *U*nit and sounds like it, too.

John E. Hodge

Western University
Kansas City, Kansas

Sodium Bromide–Hydrogen Bromide–Water

To the Editor:

In the article "The Three Component System Sodium Bromide–Hydrogen Bromide–Water," by O'Brien, Kenny, and Fuxa (J. Chem. Educ., **17**, 576 (1940)), the isothermal solubility diagram for the system is represented by what appears to be a smooth curve. Since a change in solid phase takes place as the concentration of hydrogen bromide changes, a break in the curve must be present. The data plotted are neither sufficiently accurate nor sufficiently numerous to show this break clearly. Perhaps the authors intended to indicate a break, but it is definitely not clear in the printed diagram. If, as the paper suggests, a study of this system is used as a laboratory experiment, the instructor should guard against possible misconception in the minds of the students that the curve is continuous.

William E. Cadbury, Jr.

Haverford College
Haverford, Pennsylvania

To the Editor:

We regret that the diagram in our paper was not sufficiently clear to indicate a break in the solution curve. Actually, there is an inflection in this curve between hydrogen bromide concentrations of 37.21 per cent and 41.38 per cent (Nicolaev and Ravich, *J. Gen. Chem.* (U.S.S.R.), **1**, 787 (1931)). It will be noted, however, that considerably more data than that suggested in the experiment must be taken by the student if he is to find this inflection for himself.

In Reference 1 of this paper, the page numbers should read 573–4, instead of 533–4.

S. James O'Brien

The Creighton University
Omaha, Nebraska

Copying Devices with an Argus Camera

To the Editor:

An apparatus for copying photographs and drawings on 35-mm. film in making 2″ × 2″ lantern slides is described in J. CHEM. EDUC., **16**, 308 (1939); also, a device for copying 2″ × 2″ lantern slides from $3^1/_4$″ × 4″ slides. The specifications in Figures 1 and 2 of that article are for a Leica camera. I have since had occasion to construct similar devices for use with an Argus camera, model C; and since the cost of the latter is considerably less than a Leica camera, the following data may be of some service.

The *device for making 2″ × 2″ slides from $3^1/_4$″ × 4″ slides* has the same dimensions as for a Leica camera, with the exception that the opening over which the large slide is placed should be $2^1/_8$″ × $3^1/_4$″; and the side of the camera box (not the lens) should be eight inches above the emulsion of the slide to be copied.

Dimensions for the *autofocusing copying device* are identical with those for the Leica camera with the following exceptions. The lamps should be ten, not fourteen, inches above the copying board. In place of front lenses, three collars are used: $^1/_2$-inch and one-inch collars which may be ordered from any Argus dealer ($1.00 each), and a $^1/_4$-inch collar which must be made to order. Changes in sizes of masks, and distance between the surface of the picture to be copied and the edge of the Argus camera box (again, not to the lens) are indicated in the following table.

Position of lens	*Collar in inches*	*Height, in inches, of camera edge above picture*	*Size of mask in inches*	*Number of mask*
Out	$1^1/_2$	$6^1/_2$	$1^1/_8$ × $1^3/_4$	1
(In)	($1^1/_2$)	($6^3/_4$)	($1^3/_8$ × 2)	—
(Out)	(1)	($7^1/_2$)	($1^3/_4$ × $2^3/_8$)	—
In	1	8	$2^1/_8$ × $3^1/_4$	2
(Out)	($^1/_2$)	($9^3/_4$)	(3 × $4^1/_2$)	(3)
In	$^1/_2$	$11^1/_2$	4 × 6	3
Out	$^1/_4$	$11^1/_2$	4 × 6	3
In	$^1/_4$	16	6 × 9	4

It will be noticed that the dimensions have been so chosen that mask number 3 may conveniently be used with either the $^1/_2$-inch or the $^1/_4$-inch collar. Also, by painting lines on this same mask to correspond with the size 3″ × $4^1/_2$″, it may be used for two sizes of pictures depending upon the "in" or "out" position of the lens. Exposures are of the same order as indicated in the original article.

By the use of a supplementary front lens ($1.00) still larger pictures may be copied. For example, with the copying lens attached, and with the front lens to the "out" position, camera elevation $22^1/_2$″, a picture $9^1/_2$″ × $14^3/_4$″ is in focus.

With these devices, which cost under thirty-five dollars for materials, including camera, a novice can make his own slides for a few cents apiece.

HUBERT N. ALYEA

PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY

Symbols or Abbreviations?

To the Editor:

The letter from C. E. Ronneberg, on page 44 of the January issue, is very interesting. It seems to me that the symbol "gm" is preferable to "g" for the word "gram" because of the prevailing use of "g" for the acceleration due to gravity.

I would like to suggest the use of "mM" for "millimole" and "mE" for "milliequivalent." The symbol "*N*" seems to be good for "normal" because the italicization differentiates it from "N," the symbol for "nitrogen." A similar symbol "*M*" is used for "molar."

The spelling of "mole" is preferred to "mol" because of the significance of the ending "ol" as used in organic nomenclature. The ending "ol" should be reserved for the designation of the hydroxyl group.

L. P. BIEFELD

PURDUE UNIVERSITY
LAFAYETTE, INDIANA

Oblivion?

To the Editor:

Your editorial in the January number of the JOURNAL OF CHEMICAL EDUCATION certainly strikes a responsive chord in me. It happens to be one of my favorite themes.

In a paper in this JOURNAL (**15**, 541 (Nov., 1938)) I suggested the elimination of the arc process for the fixation of nitrogen, the Le Blanc process for the manufacture of soda ash, the idea of nascent elements, the idea that oxygen and oxygen only supports combustion. I would add to these the following topics as nominations for oblivion: hydrogen peroxide, ozone, the Law of Dulong and Petit, valence as ordinarily presented in the early stages of general chemistry, and ionization tables for electrolytes based on conductance.

I also have a suspicion that we have given Dalton a lot of credit for an atomic theory that he does not deserve. I do not think he should be relegated to oblivion, but he ought to be put in his proper place.

GRAHAM COOK

ALBRIGHT COLLEGE
READING, PENNSYLVANIA

CORRECTION

A CORRECTION for "Labels in Calculations of Quantitative Chemical Analysis," in the January issue, page 36: "The liter equals 1.00028 cubic meters" should read "The liter equals 1.00028 cubic *deci*meters."

Out of the Editor's Basket

THE Committee on Motor Fuels of the American Petroleum Institute has recently published a pamphlet entitled "Power Alcohol," which is the latest word on the negative side of the controversy over the use of alcohol in motor fuels. It represents the findings of a five-year study by the Committee involving an analysis of publications, reports, and original research. It is estimated that a mixture containing ten per cent alcohol would cost three cents a gallon more than straight gasoline, and it is claimed that no purported technical advantages of such a mixture justify this extra cost. It is also stated that the alcohol scheme is actually against farm interests, rather than for them, "because farmers buy one-fourth of the motor fuel consumed, because relatively few could actually sell products to alcohol distilleries, and because of adverse influence on sales of other products, on soil fertility, and on independent farming."

● Several interesting bits of information have come to our desk recently concerning the newly developed electron microscope. We expect to carry in the next number a last-minute and first-hand account of this instrument, written by one of our own staff.

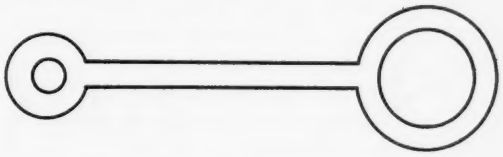
● From the Freeport Sulfur Company comes the reassuring news that the prospect of an adequate supply of sulfur for the thousands of operations vital to the arming of the nation is not today a major worry, as it was for the War Industries Board in 1918. It is estimated that a production of 3,000,000 tons a year would be necessary to maintain an army of 2,000,000 men and meet normal civilian needs in addition. We are assured that the American sulfur industry can do this, and meet present export demands as well.

● Rubber is still "rubber," because it *rubs*. But tests which were made on Ameripol, the synthetic rubber now being used in the first synthetic tires, led to the following comment:

"Certain stocks of synthetic rubber in a crude state will do a fair job of rubbing out pencil marks, and full compounding would probably enable the synthetic product to equal this function of natural rubber."

● The International Nickel Company of Canada tells us that more nickel was sold in 1940 than in any previous year. Most of the increase was in the United States, where the heavy industries were stimulated to activity by the defense program. Steel uses more than fifty per cent of the nickel output, with the second largest market in the production of nickel-copper alloys, nickel silvers, Monel, malleable nickel, and Inconel. Electroplating follows, with cast iron, resistance alloys, etc., trailing.

● Arthur Furst, of San Francisco Junior College, sends the accompanying illustration of a rubber "guard," $3\frac{1}{2}''$ long, which can be cut out of an old inner tube (using cork borers for the holes), and used to attach glass stoppers to reagent bottles—thus avoiding considerable trouble and confusion.



● M. Gordon Duvall, of Anderson Township School, Cincinnati, Ohio, reports, from his own experience, the most satisfactory method of removing frozen glass stoppers, when special apparatus is not at hand: Clean the neck and stopper; cover the head of the stopper with about four layers of toweling; grasp the protected stopper-head with pliers and twist.

● We recently saw a description of some "chemical games" which looked as though they might be interesting or amusing: "Chemname," a game of matching cards bearing the common and chemical names of substances; "Precipitate," a game like "rummy," in which cards bearing names and symbols are put together to make compounds; "Elemento," a chemical variation of "bingo" involving the completion of rows of the Periodic Table.

● The fiftieth-anniversary number of *The Merck Report* (January, 1941), which can be had free from the company, contains two good articles of chemical interest: "Fifty Years' Progress in Medical Chemistry," and "Recent Advances in the Chemistry of Natural Products." The latter discusses the discovery, isolation, and synthesis of pantothenic acid, one of the constituents of the vitamin B complex.

● An item in the "Basket" in the September, 1940, number of the JOURNAL told how E. F. Degering had found that the grades of students in the front of a classroom were consistently better than those in the back. D. S. Wright, of State College High School, State College, Pennsylvania, continues the geometrical simile and says: "The visual angle subtended by a piece of apparatus grows smaller as the distance from the lecture table increases. The difficulty of seeing a lecture experiment at any distance cannot be overemphasized. Even in my small classroom, seating 28 pupils, test-tube quantities are too small to be seen from the rear seats." He suggests that the instructor try sitting in the last seat while an assistant manipulates the apparatus.

● Sales executives are finding added reason for desiring scientific or technical training for their sales force. This was brought to light by Mr. John L. Collyer, president of the B. F. Goodrich Company, who pointed out that the very multiplicity of the new laboratory synthetics is discouraging the public from making any choice from among them. To overcome this, salesgirls "should be taught enough scientific facts so that they can give the consumer an enthusiastic picture of the dollar values and utility that are the real news in synthetics."

● H. N. Alyea, of Princeton, one of our experts on lecture demonstrations, comments as follows on the CO_2 demonstration by Wolf, described in the "Basket" in the December, 1940, number: The block of dry ice must be placed in the jar half an hour before it is to be used, or the CO_2 gas will not fill the jar completely. It is unimportant to remove the CO_2 in the breath. The most spectacular part of the experiment was not mentioned: after the bubble is floating on the CO_2, pick up the jar and walk around the room with it. The bubble meekly follows, floating in the moving jar.

RECENT BOOKS

A LABORATORY HANDBOOK AND SYLLABUS FOR A FIRST YEAR COURSE IN CHEMISTRY. *R. M. Whittaker*, Assistant Professor of Chemistry, Queens College. Department of Chemistry, Queens College, New York City, 1940. 548 pp. 23 figs. 15 × 23 cm. $1.00.

The author proposes "(1) to provide a series of laboratory experiments that can be used with any of the standard first-year college texts in chemistry; (2) to provide a series of report blanks, the completion of which will train the student in the art of observation; (3) to provide a series of problems relating to the subject matter of each unit; (4) to provide a syllabus in the form of study questions to guide the student through the voluminous subject matter of the first-year course; (5) to provide discussions on specialized subjects."

The author has provided in thirty-two units—one for each week—the usual laboratory experiments of a first-year college course in chemistry. The records of observations in the form of answers to questions or data sheets are to be torn out of the manual and submitted at the completion of the unit. A simple scheme of qualitative analysis is given under one unit and the reactions of each ion under the unit concerning the ion. Very little attention is given to the reactions of the metal as such. The manual is intended to be used with a chemistry kit and the materials needed are so arranged. The additional materials for class use are specified by experiment.

The manual is well written. The theory is modern. It should be of value to a teacher who is very busy and needs a combined workbook, manual, and study guide.

RUFUS D. REED

NEW JERSEY STATE TEACHERS COLLEGE
MONTCLAIR, NEW JERSEY

THERMODYNAMICS FOR CHEMICAL ENGINEERS. *Harold C. Weber*, Associate Professor of Chemical Engineering, Massachusetts Institute of Technology. John Wiley and Sons, Inc., New York City, 1939. vii + 264 pp. 102 figs. 15 × 23 cm. $3.25.

The preface states, "In this book an attempt has been made to present the more important thermodynamic relations in a manner particularly useful to the chemical engineer." The impression is given that the book is designed for undergraduate courses in chemical engineering curricula. This is the first book on thermodynamics written especially for the needs of chemical engineers, and the author deserves a great deal of credit for pioneering in this field. The author has succeeded in bringing together in logical sequence the principal thermodynamic ideas of chemical and of mechanical engineering thermodynamics. It is evident that he was working against space limitations; throughout the whole book one receives the impression that much in the way of explanation and derivation has been left out.

The book omits some thermodynamic aspects of particular interest to chemical engineers, such as the rigorous thermodynamics of solutions as applied in the construction of enthalpy-concentration charts known as Merkel and Ponchon diagrams, which are useful in evaporation and distillation.

The book should be satisfactory for an undergraduate text if the course is taught by a chemical engineer with a much more extended knowledge of thermodynamics than the contents of the book. The brevity of explanation might be a positive advantage to such a teacher, as it leaves to him the possibility of steering student discussion of these matters to a logical conclusion and of filling in some of the desirable material which is not included in the book.

ALBERT B. NEWMAN

COLLEGE OF THE CITY OF NEW YORK
NEW YORK CITY

FUNDAMENTALS OF CHEMISTRY. *H. G. Deming*, Professor of Chemistry, University of Nebraska. John Wiley and Sons, Inc., New York City, 1940. xiii + 756 pp. 195 figs. 15 × 23 cm. $3.50.

We have a feeling that this is the book for which many teachers of general chemistry have been unconsciously waiting, and believe that it would have been widely adopted this year if it had appeared in time. Some of its features which will commend it to those who are trying to keep their courses from stagnating are: a marked emphasis on the physico-chemical principles; a definite break with the old traditional sequence, oxygen-hydrogen-water-solutions-halogens-acids-ionization-sulfur-nitrogen-etc.; introduction of the descriptive chemistry of particular elements when it serves to illustrate general principles; an early and clear contrast between ionic and molecular compounds; a modern, but not too extreme treatment of the subject of electrolytes and the properties of acids and bases, using the Brønsted definitions; a courageous and highly successful attempt to explain some of the most recent developments; frequent use of the periodic table; emphasis upon science as a *method*. It neither insults the student's intelligence, on the one hand, nor plunges him into incomprehensible difficulties, on the other. The title is not belied in the amount of attention given to industrial processes. Technical terms are not omitted, but, after adequate definition, are often avoided by use of simpler synonyms. Altogether, it is an easy book to get enthusiastic about.

N. W. RAKESTRAW

BROWN UNIVERSITY
PROVIDENCE, RHODE ISLAND

CASEIN AND ITS INDUSTRIAL APPLICATIONS. *E. Sutermeister and F. L. Browne.* Reinhold Publishing Corporation, New York City, 1939. 433 pp. 15 × 23 cm. $6.50.

SCIENCE READING MATERIALS FOR PUPILS AND TEACHERS—III. *Clarence M. Pruitt.* Reprinted from Science Education, February, 1939. Vol. 23, No. 2, pp. 87–102. 17.5 × 26.5 cm. $0.25.

ELEMENTARY QUANTITATIVE ANALYSIS—THEORY AND PRACTICE. *H. H. Willard*, Ph.D., Professor of Analytical Chemistry, University of Michigan, and *N. H. Furman*, Ph.D., Professor of Chemistry, Princeton University. Third Edition. D. Van Nostrand and Company, Inc., New York City, 1940. x + 531 pp. 62 figs. 14 × 22 cm. $3.25.

This well-known and popular text is primarily adapted to serve as manual and brief reference book for a first year's work in quantitative analysis. The present third edition appears just seven years after the first, and represents, as did the second, a considerable modification and improvement of its predecessor. The arrangement is as follows:

Two preliminary chapters outline the scope of the subject and introduce the common laboratory operations. The third chapter discusses the balance, weighing, and calibration and introduces the first experiment (drying a salt). There are then two chapters on measurements, computations, and fundamental laws and theories. After this preliminary ninety pages come volumetric analysis, calibration, and two very thorough chapters on neutralizations. Volumetric precipitations and complex formation are followed by a long section (five chapters) on oxidation-reduction reactions.

Gravimetric analysis is next discussed and finally electrolytic and colorimetric methods. Twenty-five pages of tables, references, etc., form the appendix, which includes a five place logarithm table.

The method of presentation runs throughout from the general to the particular. First a general discussion is given, then some special method is described, its errors and difficulties discussed, and finally a detailed procedure is given. In many cases this is followed by further special modifications of the method.

The discussions are clear, logical, and instructive, and the procedures for the most part very detailed and thorough. Many of them show the effect of personal study by the authors, and in many other cases worth-while suggestions for modification are taken from the recent literature, with adequate references. The book is definitely a text rather than a comprehensive work, but few students could master all its discussions and procedures in the course of a year. As its success has indicated, this book meets the needs of a good university course, and can also be advantageously used to accompany briefer manuals or courses of lectures.

The problems seem to have been improved over previous editions.

NORRIS F. HALL

UNIVERSITY OF WISCONSIN
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ELEMENTARY LABORATORY EXPERIMENTS IN ORGANIC CHEMISTRY. *R. Adams*, Professor of Organic Chemistry, University of Illinois, and *J. R. Johnson*, Professor of Organic Chemistry, Cornell University. Third Edition. The Macmillan Company, New York City, 1940. xvi + 420 pp. 24 figs. 14 × 21 cm. $2.00.

This third edition of a well-known laboratory manual continues the policy set forth in the first edition of 1928. It is "designed for beginning students in organic chemistry whether they are specializing in chemistry or are merely seeking a knowledge of the subject for use in medicine, agriculture, home economics, biology, or related fields."

The present volume is not so much a revision, as an extension, of the second edition (1933), containing fifty-seven pages more. The additional space is used, in part, for the expansion of some of the introductory sections dealing with laboratory operations and technic, for the addition of discussions on theoretical and practical points, and the inclusion of procedures for the identification of compounds.

The section on polymerization and depolymerization will meet a desire, often expressed by students, to work with modern polymers and resins. The new syntheses of aspirin and sulfanilamide will interest students who want to learn, at first hand, about medicinals coming from the chemical laboratory. The addition of syntheses for cyclohexene and cyclohexanone emphasizes the importance of the chemistry of alicyclic compounds. It is good to see the introduction of two new preparations requiring oxidation, namely, the conversion of cyclohexanol to cyclohexanone, by the usual means of chromic acid, and the transformation of furfural to fumaric acid by the use of sodium chlorate in the presence of vanadium pentoxide as a catalyst. Very properly, attention is called to the possibility of an explosion in this second oxidation. It is the belief of the reviewer that this point cannot be emphasized too strongly.

An important addition to the book is the more adequate explanation of the treatment of burns and of the procedure to be followed in the case of accidents.

AVERY A. ASHDOWN

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THEORETICAL ELECTROCHEMISTRY. *N. A. McKenna*, B.A. (Oxon). Macmillan and Co., Ltd., London, 1939. xiii + 469 pp. 109 figs. 13.5 × 21.5 cm. 15 shillings.

This book does not cover some of the subjects found in other recent works on electrochemistry, nor does it include the matured opinions of a specialist who has long contributed to research in the field. It is a good summary of those subjects which are most commonly included in courses in physics and electrochemistry. The graduate student preparing himself for research and other more advanced readers will find this a convenient review of old material and a good introduction to recent work. So little mathematics is used that the reader may expect to understand 90–95 per cent of the book without studious effort. It is, therefore, excellent for a rapid general survey of the whole subject before the start of serious work with research reports in the original literature. The literature study will be somewhat facilitated by numerous references.

The author has been careful to distinguish between "irreversible properties," and "thermodynamic or reversible" properties. The former group includes functions such as conductivity, viscosity, and diffusion; the latter class includes activity and osmotic coefficients, electrode potentials, heat content, heat capacity, surface tension, compressibility, solubility, etc. This emphasis may help some readers who might otherwise miss this important distinction.

Much time and effort have obviously been expended in producing a book so nearly complete and well arranged, and so interesting as is this one. There are signs of hurry, however, in the finishing of the book. There are numerous errors in detail too trivial to list here, such as inconsistent or incomplete units (dimensions), the use of terms not previously defined, etc.

Especially distinctive and valuable features of the book are the four well-written chapters devoted to equilibria in solutions of weak electrolytes.

The reviewer enthusiastically welcomes this addition to the literature of electrochemistry and the thermodynamics of solutions; he recommends the book to graduate students and to others. He hopes that the author will, when it becomes necessary, revise his book to bring it up to date, and in doing so, correct the errors which now detract somewhat from it.

T. F. YOUNG

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THE NATURE OF CRYSTALS. *A. G. Ward*, B.A., Scholar of Trinity College, Cambridge. Chemical Publishing Co., Inc., New York City, 1939. vii + 114 pp. 52 figs. and 4 plates. 12 × 19 cm. $1.50.

This is a popular yet accurate account of the immense advances of the last twenty-five years in our knowledge of the structure of crystals, largely acquired through the method of X-ray analysis developed by Sir William Bragg. After a discussion of the history of crystallography, and the theoretical aspects of molecular structure, the author takes up ionic, homopolar, metallic, and molecular crystals, and the physical properties of crystals. Experiments and instructions for making models are given, which can bring the discussion home to the reader.

TEXTBOOK OF PHYSICAL CHEMISTRY. *S. Glasstone*, D.Sc., Ph.D., Princeton University. D. Van Nostrand Co., Inc., New York City, 1940. xiii + 1289 pp. 266 figs. 205 tables. 15.2 × 23.5 cm. $10.00. (Special edition available to teachers and students only, $7.50.)

Here is a book which can be recommended unreservedly for the desk use of undergraduates and graduate students, secondary-school and college teachers, and research workers. So far as difficulty is concerned, there is no reason why this textbook would not be entirely suitable for the college course in physical chemistry, provided judgment was exercised in the selection of topics. Although its bulk might terrify the undergraduate, an examination of the contents discloses that the author has accomplished his object, which, in his own words, "is to take the student with a very elementary knowledge of physical chemistry, such as might be gained in a normal course on *general chemistry*, and lead him by easy stages and with the simplest mathematical methods to such an understanding of the subject as will permit him to appreciate the more advanced treatises and recent journal literature."

The author has avoided a number of difficulties by not attempting to "graft the more recent concepts on to a background of classical ideas." The result is a thoroughly modern, consistent, and progressively developed survey of the entire field of physical chemistry. In order not to lose sight of the historical development of chemistry, however, at the end of each chapter he has provided a list of references to papers of signal historical moment, review articles, and summaries of recent developments. These enable the serious student to place particular topics in the correct perspective. Relatively difficult material and mathematical derivations are printed in small type, as are the descriptions of experimental methods. Those who are familiar with his previous books know that Dr. Glasstone writes with facility, having the ability to discuss obscure subject matter with preciseness and clarity. His style continues to be eminently readable, and while this textbook is in no sense a popularization of physical chemistry, its value is greatly enhanced by the lucid presentation.

LAURENCE S. FOSTER

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WHAT IS STEEL? *L. Scheer*, translated from the German by *F. L. Meyenberg*. Third Revised Edition. Chemical Publishing Co., Inc., New York City, 1939. xiv + 164 pp. 48 figs. and 1 diagram. 13.5 × 21.5 cm. $3.00.

The author gives a clear, concise, yet adequate discussion of the nature of steel, starting with a survey of the physics of atoms and of the space-lattice of iron, then going through the heat treatment of steel, and ending with a discussion of the numerous alloys and their uses. The work is not a book of reference, but an introduction to the subject, intended for the layman.

GROWING PLANTS WITHOUT SOIL. *D. R. Matlin*, M.A., Belmont Evening High School, Los Angeles. Chemical Publishing Co., Inc., New York City, 1939. 137 pp. 15 figs. 13.5 × 21.8 cm. $2.00.

Dealing simply and clearly with a subject of interest to many, this discussion of plant chemiculture gives the history of soilless gardening, the advantages of such a procedure, and detailed instructions for such experiments. Plant food deficiency symptoms are described, and directions given for treatment with plant growth hormone.

THE NATURE OF THE ATOM. *G. K. T. Conn*, M.A., B.A., Ph.D. Chemical Publishing Co., Inc., New York City, 1939. 115 pp. 15 figs. and 3 plates. 12 × 19 cm. $1.50.

This book discusses, in a manner intended for the layman, the atomic theory, atom models, the optical spectrum, the quantum theory, the Bohr atom, the atomic nucleus, and the periodic classification of the elements. It is simply, not exhaustively done, yet covers the main aspects of the subject intelligently.

FUNDAMENTALS OF SEMI-MICRO QUALITATIVE ANALYSIS. *E. B. Kelsey* and *H. G. Dietrich*, Assistant Professors, Yale University. The Macmillan Company, New York City, 1940. x + 350 pp. 112 figs. 14 × 21.5 cm. $2.75.

This text, like others in qualitative analysis, consists of two major parts, one on theory, of 173 pages, and the other on laboratory procedures, with introductory description of the properties of the various commonly occurring ions; in the latter section 87, 36, and 8 pages are devoted, respectively, to (1) the cations, (2) anions, and (3) solids, metals, and alloys. The usual subjects of salts, acids, bases, equilibrium, complex ions, and oxidation-reduction comprise the theoretical portion. The interionic attraction theory is given to supplement the Arrhenius theory. The newer acid-base concepts of Brønsted and Lowry are used and preferred over the older ones and reactions are written in the body of the text with the understanding that the solvent, though playing its part, is not shown.

Each chapter is followed by excellent sets of exercises or problems, and many have a short list of up-to-date collateral reading. In the theory portion the subjects are treated briefly, yet sufficiently extensively to give the student all needed information. Semimicro technics are used in the analytical procedures, but too much is left to the discretion of teacher and student as to the design and proper use of equipment. Teachers unfamiliar with these technics may have difficulties because of this. Throughout all procedures quantitative portions of solutions of known strength are prescribed, thus eliminating much guesswork. The inclusion of numerous "preliminary experiments" the authors believe "leads to the waste of a inordinate amount of the student's time" and therefore these do not generally appear in the book.

The customary methods of separation, in general, are used throughout the analytical procedures. Organic reagents have been used, but largely for confirmation tests. A short appendix gives a list of apparatus, reagents, composition of practice solutions, solubility and logarithm tables.

The purpose of the text—a better means for teaching fundamentals of analysis—necessitates a larger volume than can be used as part of the usual year of general chemistry, but it seems admirably adapted for a semester or quarter course in qualitative analysis. The authors may be commended for the simple, clear language used, which should be readily understood by the average student.

O. M. SMITH

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NEW WORLD OF CHEMISTRY. *B. Jaffe*, Bushwick High School. Fourth Edition. Silver Burdett Company, New York City, 1940. xi + 692 pp. 14 × 20.5 cm. $1.84.

A different elementary textbook, written by a man who has already shown his ability to write vividly and dramatically. Student interest is assured by the inclusion of significant historical material, showing the part played by science in the development of modern civilization. Consumer chemistry and the chemistry of common things are emphasized, reflecting the trend toward a more socialized science. Yet throughout the NEW WORLD OF CHEMISTRY the laws of conservation of matter and conservation of energy, and the electron theory of matter and the theory of ionization, are basic; the fundamental tools of chemistry—valence, the formula, the equation, and the solution of problems, are introduced early into the text and used throughout. Photographs and illustrations are graphic. For those to whom chemistry might be a bitter pill, this book gives a sugar coating which wears well; yet it does the work just as efficiently.

THE CHEMICAL FORMULARY. *H. Bennett, Editor-in-chief*. Chemical Publishing Company of New York City, Inc., 1939. 638 pp. 13.5 × 22 cm. $6.00.

HOW TO MAKE AND USE A SMALL CHEMICAL LABORATORY. *Raymond Francis Yates*, revised and enlarged by *S. A. Pellerano*. The Norman W. Henley Publishing Company, New York City, 1939. 46 pp. 12.5 × 19 cm. $1.00.

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J. E. BELCHER and J. C. COLBERT

Assistant Professors of Chemistry
University of Oklahoma

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The following excerpt from the January, 1941, issue of the "Cenco News Chats" is self-explanatory.

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Further information may be had by writing the *Central Scientific Company, 1700 Irving Park Blvd., Chicago, Ill.*

Coal Tar Chemicals

A 51-page booklet entitled "Coal Tar Chemicals" recently released by the Reilly Tar & Chemical Corporation describes many coal tar chemicals offered by them. In the acknowledgment of responsibility, the company claims that most of the products listed in the booklet are now being produced in commercial quantities by some or all of the Reilly Company's fifteen major plants, and that some have not yet reached the stage of quantity production, but they are now made available for use in further research and development.

In addition to some special items classified as "Reilly products" the following chemicals are included in the booklet: Acenaphthene, Acridine, 2-Aminopyridine, 2-Methyl-6-Aminopyridine, Anthracene, Coal Tar Bases, Carbazole, U. S. P. Cresol, Meta Cresol, Ortho Cresol, Para Cresol, Cresylic Acid, High Coefficient Acid, Dimethylnaphthalene, Diphenylene Oxide (Dibenzofuran), Fluoranthene, Fluorene, 2,6-Lutidine, Alpha-Beta Methylnaphthalene, 1-Methylnaphthalene, 2-Methylnaphthalene, Naphthalene, Phenanthrene, Phenol, Alpha Picoline, Beta Picoline, Pyrene, Pyridine, Quinoline, Xylenols, 1,3,5-Xylenol.

This booklet may be obtained by writing to the *Reilly Tar & Chemical Corporation, Indianapolis, Indiana.*

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A transparent plastic pump for handling dilute acids, hypochlorites and many other chemicals, is being marketed by the *Milton Roy Company, Philadelphia.*

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Further information regarding this item may be obtained by writing to the *Milton Roy Company.*

Electric Heating Equipment Catalog

A new catalog on electric heating equipment is available from *Cooley Electric Manufacturing Corporation, 215 South Senate Avenue, Indianapolis, Ind.* The catalog illustrates and describes their line of muffle furnaces, combustion tube furnaces, and hot plates. Copies are available free on request.

Taylor Instrument Company Publication

"Taylor-Rochester," a publication of the Taylor Instrument Co. may be obtained by schools, colleges, and libraries, either through librarians or instructors (official stationery should be used in writing).

Typical of the articles therein are the following taken from the contents of Vol. XXX No. 2: Old Man Winter's Prank cost Millions; South Florida's Freeze; Blue Ridge Parkway's only Town; Weather Stations "planted" in Mid-Ocean; Extremes in Temperature develop New Market for Food Stuffs; The Thirst of Plant Life; Terrain Clearance Altimeter, Perfected; Alaska—Oasis of a Former Day; Galveston—a Wonder City; Fire-Clay Mortars defy High Temperatures; Water and Its Various Forms; Temperature Extremes in Space; Fighting High-Heat Building Fires with Chemicals.

For further information, address *Taylor Instrument Companies, Rochester, New York.*